INSTITUTE NOTES.

SEPTEMBER, 1940.

STUDENTS' MEDAL AND PRIZE.

The Council has awarded the Students' Medal and Prize to Mr. T. Y. Ju, Stud.Inst.Pet. (Birmingham University), for an essay on "Behaviour of Fuels in C.I. Engines."

A Special Prize has also been awarded to Mr. D. G. Brunner, Stud.Inst.Pet. (Birmingham University), for an essay on "Mud Fluids for Drilling."

B. A. Murphy (Melbourne) and P. G. Owen (Birmingham University) have been highly commended for their essays.

NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws, Section IV, Para. 7.

Elections are subject to confirmation in accordance with the By-Laws, Section IV, paras. 9 and 10.

As Fellows.

BROWN, Norman Fraser	Burma.
KUHN, Wayne Edward	New York.
PRUTTON, Carl F.	Cleveland, Ohio.
SMITH, Roland Wilfred John	Shell Haven.
SUTER, Hans H.	Trinidad.

Transfer to Fellows.

HUNTER, Thomas Girvan	Birmingham.
KEIGHTLEY, Walter Allison	London.
LEWIS, Robert Illtyd	Teddington.

As Members.

ALLEN, Eric Edgerton	Anglesey.
ALLEN, Sydney Hugh	Leeds.
MILLS, Leonard	Ormskirk.
MOON, Alec	Pinner.
MOORE, Lancelot Frederick	East Moseley.
SMITH, James Edward	Trinidad.
STOTT, Victor Howard	Manchester.
THOMPSON, John Rennet	Manchester.
TULLY, James	Thropton (Northumberland).
YONGE, Dudley Arthur	Chester.

Transfer to Member.

COOPER, Arundel David	Egypt.

As Associate Members.

AGOSTINI, Pierre Leon	Trinidad.
GIBBS, Eric Clarence	London.
PEASE, Sherman Levi	Minneapolis.
PINDER, John Cuthbert	Nottingham.
ROUGHSEDGE, Norman Donovan	Sunderland.
SIMPSON, Michael John	Teddington.

Transfer to Associate Members.

HAWORTH, Alfred John	Burma.
PACHACHI, Nadim	Iraq.

As Student.

PYMAN, Lawrence Lee	Cranwell.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

BAARS, Gerrit., Chemical Engineer, c/o Mrs. Bailey, Edgerton House, Great Sutton, Wirral. (*J. A. Oriel ; H. LeQ. Herbert.*)

BUSH, Sydney Steve, Technical Representative (*Shell-Mex & B.P., Ltd.*), 41, Weymouth Avenue, Ealing, W.5. (*A. E. Hope ; F. N. Harrap.*)

DAVIDSON, Anthony Dryden, B.Sc., Chemical Engineer, c/o Foster Wheeler, Ltd., Aldwych House, Aldwych, London, W.C. 2. (*A. W. Nash ; R. K. Fischer.*)

FLETCHER, Charles Horace, Mechanical Engr. and Driller, A.T.M.N., Ltd., P.O., Barakin Ladi, Northern Nigeria, W.A.

HOLE, Herbert Wray, General Manager, New Brunswick Gas & Oil Fields, Canada. (*C. A. P. Southwell ; A. E. Dunstan.*) (*Trans. to Fellow.*)

HUBLEY, John Stuart, B.Sc., Refinery Operator, Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (*B. G. Banks ; J. T. T. Robinson.*)

JOHNSTON, Douglas Gordon, Lubrication Engr. (*The Texas Oil Co.*), 185, Welling Way, Welling, Kent. (*N. L. Anfilogoff ; W. A. Webster.*)

KEACH, Raymond Harry, B.Sc., Chemical Engr., Foster Wheeler, Ltd., Aldwych House, London, W.C. 2. (*A. W. Nash ; R. K. Fischer.*) (*Trans. to A.M.*)

LANGDON, Charles Ernest James, B.Sc., Chemist, 32, Moor Mead Road, Twickenham, Middx. (*Dr. Dunstan ; D. A. Howes.*)

LE BLANC-SMITH, William Leonard, Technical Representative (*Vigzol Oil Refining Co.*), "Walnut Tree Cottage," Great Barton, Nr. Bury St. Edmunds, Suffolk. (*S. Elliman ; L. Mills.*)

MARGOSCHES, Charles G., Ing.-Dr., Research Chemist, 113, Hubert Grove, London, S.W. 9. (*M. L. Steinschneider ; L. Singer.*)

RALPH, Noël Albert, Works Chemist (*Horton Manufacturing Co.*), 7, Frankland Close, Croxley Green, Herts.

WARD, Stanley Allen, B.Sc., A.I.C., Chemical Engr. (*Foster Wheeler, Ltd.*), "Tresco," 7, Seaforth Gardens, Stoneleigh, Ewell, Surrey. (*R. K. Fischer ; W. H. Hoyte.*)

ARTHUR W. EASTLAKE,

Honorary Secretary.

ANNUAL REVIEWS OF PETROLEUM TECHNOLOGY

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Vol. 26. No. 203. September 1940.

PISTON DEPOSITS, RING STICKING, VARNISHING AND RING CLOGGING *

By W. A. Gruse and C. J. Livingstone.

General Principles.

The two basic chemical changes in lubricating oils which underlie the formation of engine deposits are :—

(*a*) The thermal coking of the hydrocarbons under essentially non-oxidizing conditions.

This is what occurs in the familiar carbon-residue test. Two general influences govern the amount of residue left behind by coking. One is the molecular weight of the hydrocarbons, indicated roughly by the boiling point or the viscosity at some elevated temperature, such as 210° F. As molecular weight (or boiling point or viscosity) increases in any one family of oils, the carbon residue increases. The other influence is the chemical make-up. In a comparison of several oils of about the same molecular weight, the amount of carbonaceous residue on coking increases with the proportion of ring groups, particularly aromatics, present in the oil molecules.

(*b*) The oxidation of the hydrocarbons.

This is the change involved in the Sligh, Indiana, Underwood, and British Air Ministry tests.†

The mechanism of oil oxidation is not well understood, but in general there are two basic reactions which occur. If an oil molecule is paraffinic in nature, the oxidation products will at first be acids resembling the ordinary soap acids; in engine operation these may combine with metals present to form soaps. If the conditions are such that acids of low molecular weight are obtained, combination with metals will occur more readily than if the molecules are large. Ordinarily, the higher the oxidation temperature and the longer-continued the oxidation, the smaller will be the acid molecules produced.

On the other hand, if an aromatic or partly aromatic molecule is oxidized, the oxidation products, while somewhat acid, will fall predominantly in the class of resins, and as the oxidation proceeds, the products resemble more nearly ordinary asphalt, and are known as asphaltenes. These oxidized resins and asphaltenes are much more unstable on heating than are the oils from which they have been formed. Therefore they decompose

* Paper received 15th June, 1940.

† Sligh, *Proc. A.S.T.M.*, 1927, **27**, Part I, p. 461.
Indiana: T. H. Rogers and B. H. Shoemaker, *Indust. Engng Chem., Anal. Ed.*, 15th Nov., 1934, **6**, No. 6, pp. 419–440.
Underwood: H. C. Mougey, Preprint S.A.E. World Automotive Congress, New York Meeting, 23rd May, 1939.
British Air Ministry: Garner, Keeley, and Taylor, *World Petroleum Congress, London* (1933) *Proceedings*, Vol. II, p. 448.

easily on further heating, yielding products of still higher carbon content and more solid consistency.

One fact of real significance about all these oxidation products is that as their molecular weight increases, they become more insoluble in all kinds of oils. This applies particularly to the soaps formed by oxidation of paraffinic oils, and to the resins and asphaltenes from aromatic and semi-aromatic oils. It applies all the more to the products of thermal cracking of the oxidized compounds.

Another significant fact depends on the difference in solvent power for oxidation products (particularly resins and asphaltenes) shown by different kinds of oils. The paraffinic oils are poor solvents, the aromatic relatively good solvents, and the semi-aromatic fall between.

Three physical changes which can and do occur in engine operation are important to the forming of engine deposits :—

(*a*) The evaporation, at moderate engine temperatures, of the lower-boiling (SAE 10 and 20) oils when they carry oxidation products in solution. While these oils boil normally under atmospheric pressure in the range 650–950° F., it should not be forgotten that at several locations in an engine they are spread in thin films and are exposed to the passage of blow-by gases. Under these conditions the ordinary vapour-pressure characteristics may cease to apply, so that evaporation will occur more readily. When such evaporation does occur, any dissolved oxidation products will be left behind on the evaporating surface, just as dissolved shellac is left behind when the solvent alcohol evaporates.

(*b*) The precipitation of products which have become insoluble because they have increased in concentration beyond the solubility limits, or because they have changed in chemical constitution. The first applies to the gradual accumulation of soaps, resins, and asphaltenes in oils undergoing crank-case oxidation. The concentration will increase until a limit is passed and a precipitate appears, usually as an asphaltic mud. As suggested, a paraffinic oil will tolerate much less dissolved material of this sort than will an aromatic oil. The second is exemplified by the separation from an oxidized oil, on heating, of decomposition products formed from oxidized compounds which were soluble until heated. With aromatic oils this separated product is likely to be first a sticky tar which becomes solid when cooled. It decomposes on further heating to a friable semi-solid which will not melt.

(*c*) The formation of emulsions of oil, usually contaminated with water, the emulsion stabilized by finely divided solids. The importance of these emulsions as such is familiar, but it is not so generally recognized that they may be dried in place, leaving voluminous granular deposits.

Ring Sticking.

The cause of this phenomenon remains obscured in a cloud of controversy. So far as any influence which the nature of the oil may have, opinion, based on both published * and unpublished information, is divided into

* Fairlie, *Oil & Gas J.*, 1936, **34**, No. 44, p. 114.
Larson, Ainsley, and Fairley, *ibid.*, 1936, **34**, No. 39, p. 24.
Rosen, *J. Soc. aut. Engrs.*, 1937, **40**, 165.

two camps. One adheres to the belief that ring-sticking tendency increases with the ease of oxidation of the oil (as indicated by laboratory oxidation tests), whilst the other believes that a volatile oil is best, ease of oxidation being relatively unimportant. The outstanding feature of the situation seems to be a large mass of contradictory experimental data. We believe this to be due chiefly to the fact that experimenters are using different types of engines under different operating conditions and that the very important mechanical details are being controlled to different extents. Each of the two opinions is undoubtedly sound, depending on the conditions under which it was deduced. In 1937 * we pointed out that either type of oil is likely to cause or not to cause ring sticking, depending on the conditions. The chemical fundamentals to be controlled are probably :—

Ring-belt temperature.
Rate of oil consumption.
Extent of oil oxidation.

A discussion of these follows, but it seems desirable to comment first on the importance of mechanical conditions and details.

Mechanical Influences on Ring Sticking.

Among these are :—

Ring-side clearance.
Uniformity of ring-side clearance.
Condition of cylinder wall surface, including ring conformation against cylinder wall.
Material, design and reproducibility of pistons.

Since these variables must be controlled in test runs, they are factors which will influence the prevalence of ring-sticking in service.†

Ring-side Clearance.

The importance of this variable is obvious, and was pointed out by the authors in the 1937 paper just mentioned. In a supercharged test engine under otherwise rigidly controlled conditions, at an arbitrary wall temperature of 345° F. at the top of the cylinder barrel, and a ring-side clearance of 0·002 in. (to an accuracy of about 30 per cent.), ring sticking occurred in a given time period with all kinds of oils. When the side clearance was increased to 0·003 in., it was possible to recognize, in the same time period, variations in the performance of different types of oils. With continued running, a certain amount of normal wear is to be anticipated, so that side clearance will increase. We agree with the belief that much trouble can be avoided in service by increasing side clearance, but it should be remembered that with long-time running a wide clearance may increase to the point where harmful fluttering or surging may occur.

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* "A.S.T.M. Symposium on Lubricants," 1937, p. 13.

† Since this paper was presented, the importance of variable distortion of pistons when heated has been pointed out to us by A. L. Heintze and C. G. A. Rosen.

Uniformity of Side Clearance.

Uniform side clearance around the piston is obviously important. In order to avoid the normal increase in side clearance observed with aluminum pistons, we have done much of our work with cast iron. In one case we noted a gradual increase in sticking tendency of the top ring, when conditions were apparently unchanged from one test run to another; this was traced to an increase (by wear of the top land) in side clearance at one point in the circumference amounting to about 0·0022 in., compared with 0·0005 in. at a point opposite. A plot of the measurements around the groove is given in the accompanying Fig. 1. An examination of the diagram shows that opposite the exhaust valve the ring could not seat against the land. A path was thus open for hot blow-by gases to pass behind the ring and to decompose, into an adhesive cement, whatever oil products were there. This effect persisted even when cylinder wall temperature was lowered 100° F.

Condition of Cylinder Wall Surface.

At one point we encountered a very puzzling sequence of results. These are represented in the following tabulation. All conditions were rigidly controlled, sticking being induced by supercharging and a reproduced high wall temperature. The two oils used were of the same type, highly refined paraffinic. A new top ring was used in each run, the lower rings being retained to keep oil consumption the same.

Oil.	Oil consumption.	Sticking observed.
S.A.E. 40	10 gm./hr.	Top ring stuck; others free.
	This run repeated several times in succession with identical results.	
S.A.E. 20	9 gm./hr.	Top ring stuck; others free.
S.A.E. 20	39 gm./hr.	Top ring free; second ring stuck.
	Repeated several times with identical results.	
	(Run-in period, light load, on set of Ferrox rings; Ferrox rings then removed.)	
S.A.E. 20	19 gm./hr.	Top ring stuck.
S.A.E. 20	40 gm./hr.	Top ring free; second ring stuck.
S.A.E. 40	46 gm./hr.	Top ring free; second ring stuck.
S.A.E. 40	39 gm./hr.	Top ring stuck; second ring stuck.
S.A.E. 40	10 gm./hr.	Top ring stuck; others free.

The explanation of this sequence, as we worked it out, was as follows: the S.A.E. 40 oil formed a satisfactory lubricating film and left the cylinder wall in good condition. The oil consumption was low and the top ring stuck. The first run with S.A.E. 20 found the wall in good condition, and this lasted for the period of the test; oil consumption remained low. However, the viscosity of the S.A.E. 20 was not sufficient to maintain good lubrication very long at the prevailing wall temperature, and the second run with the 20 oil was sufficient to scuff the cylinder walls; oil consumption then went up sharply. This condition continued during repeated runs with the S.A.E. 20 until the wall was smoothed down by a low-temperature run with Ferrox rings. This surface lasted through one run with the S.A.E.

20 oil, after which it roughed up again. At this point a test run with S.A.E. 40 oil effected the same change as had been effected in a shorter time by the Ferrox rings; however, during the polishing up the oil consumption was high. Once established, the surface maintained itself with continued use of S.A.E. 40 oil, and the test results were the same as in the first runs on S.A.E. 40.

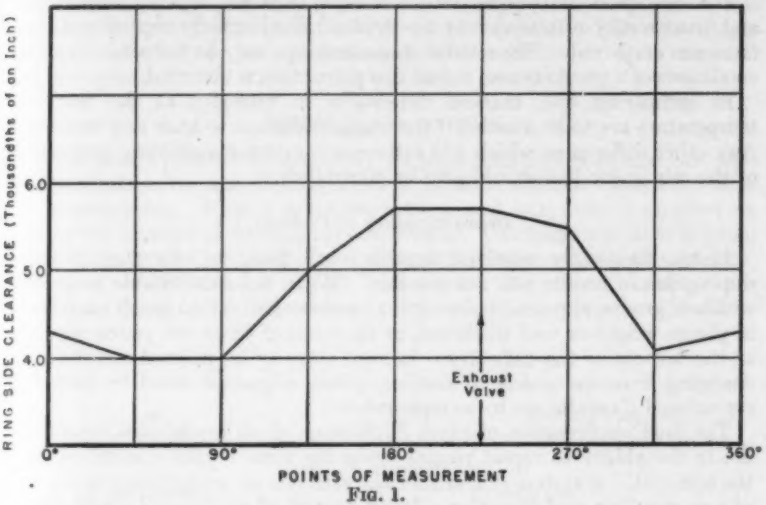

FIG. 1.

VARIATIONS IN RING SIDE CLEARANCE AFTER 195 HOURS OF RUNNING TIME. NORMAL CLEARANCE—3·5 THOUSANDTHS.

In order to confirm this explanation a second short series was made under the same conditions and with the same oils, except that the cylinder wall surface was observed by use of a profilometer.*

The results are tabulated as follows :—

	Oil consumption.	Sticking observed.	Wall condition (average roughness, micro inches).
Control run—S.A.E. 40 .	12 gm./hr.	Top stuck; others free	—
No rougher spots anywhere	—	Top of ring travel	3
		Bottom of ring travel	8
Test run—S.A.E. 20 (A) .	13 gm./hr.	Top free; second tacked	—
Repeat (B) .	10 gm./hr.	Top stuck; others free	—
Repeat (C)	30 gm./hr.	Top tacked; second stuck	—
		Top of ring travel	8
		Bottom of ring travel	13
		Spot 1·5 in. below top of ring travel, 0·75 in. in diam., under exhaust valve	20–30

* By courtesy of P. G. Exline, Gulf Research and Development Co.

Runs A and B are considered to be essentially duplicates, during which the scuffing had not advanced very far. Run C represents the incipient scuffing under discussion; continuation of this process would have ruined the cylinder wall.

The practical deductions from this series of experiments include the following points.

The condition of cylinder-wall and ring surfaces is very important, and trustworthy results cannot be obtained until exactly reproduced surfaces are employed. The results of one test run may be influenced by the conditions of a previous one, unless this precaution is observed.

In comparing oils, marked differences in viscosity at the working temperature are to be avoided if the comparisons are to have any meaning. Any other differences which will influence the film-maintaining properties of the oils under test should also be controlled.

Reproducibility of Pistons.

It has frequently occurred in this work that, on changing pistons, duplication of results was not possible. When not attributable to groove width or groove non-uniformity, it was usually found that small variations in piston weight or wall thickness, or tightness of fit on the piston pin, lay at the bottom of the difficulty. It need scarcely be pointed out that, on changing from one piston to another, piston alignment must be perfectly reproduced if results are to be repeated.

The final confirmation of exact duplication of all mechanical conditions lies in the ability to repeat results under the same engine conditions with the same oil. A system of control runs with one oil interspersed in a series of test runs is a real necessity. Rigid control of mechanical conditions is very difficult to attain, and an unbroken series of consistent results is scarcely to be expected.

Chemical Influences on Ring-sticking.

Ring-belt Temperature.

The influence of piston temperature in the ring belt has been discussed fully by Rosen.* It has been possible in our present work to confirm the general correctness of Rosen's conclusions when piston temperature was varied only by changing wall temperature, engine output remaining constant. With a given paraffinic oil and a definite set of test conditions, the following sequence was obtained :—

Relative wall temperature, ° F.	
330	Deposits formed on piston land above top ring, and behind top ring; ring itself well lubricated and wet with oil. All lower rings clear of deposit.
345	Top ring stuck tight; second ring wet with oil.
360	Top ring and groove dry and clean; not lubricated; all oil was burning off. Deposit building up on land above second ring. Lower rings wet with oil.

* *J. Soc. aut. Engrs.*, 1937, **40**, 165.

It appears from these results that a particular optimum of temperature was located at which ring-sticking occurred most readily. Below this temperature sufficient liquid oil passed through the top groove to prevent accumulation of any serious amount of deposit. The piston below this point was cool enough to avoid deposition. Above this optimum temperature oil reaching the top groove was apparently burned away, so that no deposit accumulated. Just below this point on the piston the temperature was apparently right to permit the baking out of a deposit, which accordingly formed there. This last phenomenon has been observed in aircraft-engine operation.

Rate of Oil Consumption.

From our experience in this study we have been forced to conclude that no duplication in ring-sticking work is possible without close control of oil consumption. This is not always easy, and is usually dependent on proper adjustment of mechanical conditions. The following table is based on test runs in which type of oil and oil consumption were the only variables; all other conditions were closely controlled. The results illustrate the variations likely to be encountered when oil consumption is allowed to change.

Oil.	Consumption, gm./hr.	Sticking observed.
	Low Oil Consumption.	
S.A.E. 30, solvent-refined naphthenic	15·3	All rings free.
	19·3	Top ring tacky but free; other rings free.
S.A.E. 40, paraffinic	16·8	Top stuck; others free.
	16·2	Top stuck; others free.
	11·2	Top stuck; others free.
	High Oil Consumption.	
S.A.E. 30, solvent-refined naphthenic	36·8	Top stuck; second stuck.
	100·0	Top stuck; second tacky.
S.A.E. 40, paraffinic	39·6	All rings free.
	28·0	All rings free.

It will be observed that when oil consumption was low, the naphthenic oil left the rings free, whilst the paraffinic oil produced sticking. When oil consumption, on the other hand, was high, the reverse was encountered: the naphthenic oil stuck the rings and the paraffinic left them free.

The explanation of these differences is believed to lie in the variation in behaviour of the two oils. At a low rate of flow to the ring grooves the more volatile naphthenic oil apparently vaporized away rapidly enough and cleanly enough so that no appreciable residue of an adhesive nature was left on the rings; the less volatile paraffinic oil, however, at the prevailing temperature, left behind a sticky residuum which accumulated (was probably also oxidized) and finally bound the rings. When the oil flow past

the rings was approximately doubled, however, the residue from the paraffinic oil was kept diluted, so that it flowed up rapidly, and thus never had an opportunity of attaining a firmly adhesive condition. The naphthenic oil, by contrast, at a high rate of flow, evaporated only partly; the residue in the groove evidently then oxidized to a binding cement. This set of phenomena probably represents one of the underlying reasons for the prevailing differences of opinion as to the relative merits of paraffinic and naphthenic oils in reference to ring-sticking. The proponents of naphthenic oils are probably working with engines characterized by low oil consumption as related to piston temperature and output, whilst the proponents of paraffinic oils are perhaps concerned with engines which use more oil in proportion to piston temperature. This is discussed below.

Extent of Oil Oxidation.

The significance of oil oxidation in the ring-sticking picture is very difficult to evaluate. Oxidation in the ring grooves has been suggested as involved in the explanation just given as to why change in oil consumption affects the results from different type oils in different ways. There is much evidence for the belief that accumulation of oxidation products in crankcase oil will in many cases accelerate ring-sticking, but this probably gives too simple a view of the situation; facts are not yet available for a complete discussion.

Earlier in the paper it was pointed out that two schools of thought existed with regard to the importance of oxidation tendencies of oils. These seem to be based on real experience to the effect that in some cases clean burning-off in laboratory tests will select oils which do not stick rings, whilst in other cases resistance to high-temperature oxidation tests will point out desirable oils. The obvious reason for this contradiction has been suggested above. The adherents of volatile naphthenic oils which show good burn-off characteristics seem to be concerned with engines which normally operate at oil consumptions low enough to take advantage of the clean-burning character of such oils. The adherents of the less volatile, generally oxidation-resistant paraffinic oils, by contrast, may be occupied with the lubrication of engines characterized by somewhat higher oil consumption and higher temperature, or by a more significant amount of crankcase oxidation.

In this discussion of ring-sticking phenomena only such data have been used in which it is believed that all variables were comparable except the one deliberately changed; those not familiar with such work might conclude that this condition is easy to attain. As a matter of fact, any one engaged in ring-sticking study should expect to spend a high proportion of his time in explaining to himself why his results do not check, and in locating unsuspected and uncontrolled variables. Ring-sticking is a very complex phenomenon, due in actual service to a variety of causes; it is doubtful whether any one laboratory test (engine or otherwise) can be devised to evaluate lubricating oils in a way which will correlate with all the variables in service.

VARNISH.*

The formation of varnish-like deposits, soluble in acetone and similar solvents, on engine parts, is not altogether a recent development. It has been known for years, and has usually been associated with the oxidation of oils of the sludge-forming type, and usually under conditions severe enough to cause accelerated deterioration. The fact that such deposits are being encountered in service is one indication that service conditions have become quite severe. There is not much doubt that oils differ in their tendency to form varnish. In our experimental work some years ago we encountered a striking comparison. Two oils of S.A.E. 40 viscosity were used in a prototype test engine under identical conditions and with the same amount of air fed into the crankcase. The figures for the two tests are as follows :—

	Oil A.	Oil B.
Time, hours	50	50
Crankcase temp., ° F.	280	280
Neutralization number increase	6·6	4·8
Saponification number increase	25·1	18·3
Precipitation number increase	0·02	1·6 †
Viscosity increase at 210° Saybolt sec.	686	2178
Carbon residue increase	—	2·35
Condition of engine	No crankcase, piston skirt, or ring deposits.	Crankcase sludged; all bearings and piston tightly cemented by varnish.

† This value was 3·6 at 40 hours; the decrease corresponds to rapid sludging.

An almost identical case was encountered in a comparison of two S.A.E. 20 oils of the same general type. A presumption of similarity, if not identity, for the sludge and the varnish from the unstable oil is afforded by the following data, obtained by micro-analysis :—

	Varnish.	Sludge.
Carbon, %	74·6	73·1
Hydrogen	6·9	6·7
Oxygen (diff.)	17·8	16·2
Ash	0·68	4·0

The higher ash content of the sludge might be due to the fact that the sample was obtained by scraping, whilst that of the varnish was recovered by solution in acetone.

* The authors have not included, under the term "varnish" the orange-to-black, highly adherent and insoluble coatings associated with extremely high temperature operation. For these deposits, the authors have reserved the term "lacquer"; they suggest the distinction as a useful one.

In the spring of 1938 we had occasion to investigate a series of reclaimed motor oils. The occurrence of varnish with these materials was obviously related to their content of soluble oxidation products, and we were induced to continue the study with some new oils in order to connect the phenomena of our earlier observations. The work led us to conclude that the following are controlling factors in the early formation of acetone-soluble varnish in gasoline engines :—

(1) High crankcase oil temperature. The critical temperatures are in general about the same as those which will produce corrosive acids by oil oxidation.

(2) Oxidation of the oil to compounds which will ultimately drop out of solution as sludge. The amount of varnish deposited seems to be closely proportional to the amount of oxidation effected; interrupting the oxidation will stop the depositing of varnish after the supply of oxidized products has been exhausted.

(3) Adequate solvent power on the part of the lubricating oil for the oxidation products formed. The addition of 10 per cent. of preoxidized oil to a crankcase oil of low solvent power resulted, during the ensuing test run, in the formation of crankcase sludge, but no varnishing. The addition of 10 per cent. increments of preoxidized oil was repeated twice, with 10 hours of engine running between each addition. At the end of 35 hours the engine was badly sludged, but no varnish had been formed. The addition of 10 per cent. of the same preoxidized oil to a crankcase oil of high solvent power produced during the test run a copious varnish after 5 hours' operation, with no appreciable crankcase sludge. The high-solvency oil by itself had showed no varnishing until after 10 hours of running, which indicates that it took little, if any, part in the phenomenon.

As a further confirmation of this set of phenomena, the high-grade oil of low solvent power for sludge, mentioned above, was used in an experiment in which a completely filled filter cartridge of the cotton waste type was cut into the circuit. When this was done, the oil, which had produced no varnish by itself, yielded a slight but definite varnish deposit on the piston in 10 hours of operation. It thus appears that the presence of a contaminated filter cartridge in a lubricating system may serve as a source of varnish, even though the oil being used is of such a quality as not to cause trouble by itself.

(4) A high content of easily evaporated material in the oil medium. This may be the volatile neutral oil present in some S.A.E. 10 and 20 products, or may be heavy ends of gasoline coming in as fuel diluent. In the absence of any better explanation, it would seem that the light material evaporates off from the film of oil in contact with hot surfaces, concentrating the soluble oxidation products, which deposit as varnish; the process resembles the laying down of a shellac film when the alcohol solvent evaporates.

(5) Catalytic influences of materials in contact with the oil at high crankcase temperature. A comparison of several different bearing materials in the same engine, the oil and the test conditions being the same, gave the following :—

Bearing material.	Time, hrs.	Varnish.
Copper–lead	10	Severe
Cadmium–silver	10	Severe
Babbitt	20	Slight

New bearing shells of identical size (to 0·0001 in.) were used for each test.

It is well known that oil deteriorates much faster in new engines than in those well conditioned by use; this is presumably due to the catalytic action of the fresh metal surfaces and particles. Similarly metallic soaps and other oil oxidation products will usually promote deterioration.* These influences will accelerate lacquer deposition, and should be taken into account in both research and operating control.

All the above controlling factors have been closely related to the lubricating oil and its functioning; there are, however, several ways in which the gasoline fuel can share in the responsibility for engine varnish. These are all related to the fact that gasoline is not completely burned during starting and cold operation, particularly under light load. Under these conditions the unburned fuel consists of high-boiling fractions of the gasoline, somewhat oxidized by having been compressed with air in the compression stroke and then heated by direct contact with a flame. At these high temperatures the conventional gum inhibitors used in gasolines could not be expected to prevent oxidation. The heavy ends of cracked gasolines are themselves fair solvents for oil resins, and after oxidation of this sort are still better.† Furthermore, after oxidation of this sort it is evident that the unburned heavy fractions are potential sources of gum resins, since they contain aldehydes and probably peroxides.

These partly oxidized heavy fractions of gasoline may share in varnish formation in three ways :—

(*a*) They will pass down into the crankcase by migration past the piston rings, and accumulate in the crankcase. Each increment of diluent can be evaporated away from the oil by crankcase ventilating, and this may occur many times. But each time the diluent evaporates, its non-volatile gum content will be left behind, and in this way an appreciable concentration of soluble fuel gum can be built up in the crankcase oil. This functions in a manner analogous to that of the soluble resins and other products resulting from the oxidation of the oil itself, as discussed above; it deposits as varnish on metal surfaces when rendered insoluble by heating or by evaporation of the solvent.

(*b*) Once mixed with the oil, they will increase its solvent power for soluble oxidation products deposited (perhaps harmlessly) somewhere in the engine or in the oil filter. The influence of this sequence on varnishing has been discussed above.

* The suspending action of some soaps may, of course, also be significant under certain conditions in hindering deposition.

† The back firing, through the carburettor of an engine running on gasoline with an extremely retarded spark, has been observed, in the authors' laboratory, to produce definite traces of phenol; phenol is a better solvent for resins than is gasoline, and this gives a picture of the improvement of solvent power by flame oxidation.

(*c*) Since these unburned materials are introduced above the piston, they have ample opportunity to come into contact with the piston crown and head carbon deposits formed in normal operation. When these deposits are laid down under conditions of low temperature operation, they contain a high proportion of partly burned oil, resins and asphaltenes, which serve as binders for the solids; as is well known, deposits of this type are characteristically soft and pasty. Diluent entering the crankcase under these conditions is likely to be saturated with unstable extracts from the carbon deposits, which can take part directly in the laying down of varnish.

Oil-ring Clogging and Sticking.

Two very common types of lubrication trouble during the past few years have been winter sludging and the premature increase of oil consumption in engines apparently in otherwise good condition. This latter may occur at anywhere from 10,000 to 20,000 miles of use. Winter sludging is normally common only in operations where the ratio of idling time to miles travelled is very high, but the premature rise in oil consumption is very common for passenger automobiles generally. Strikingly enough, the difficulty does not seem to occur as soon in salesmen's cars, running 50,000 miles in a year, as it does in a carefully operated family car, used 6000 to 10,000 miles annually.

The two phenomena are perhaps more closely related than is apparent. The forming of winter sludge is correctly attributed to the emulsifying of oil and water by solid carbon-like materials (see photomicrograph, Fig. 2),* and most writers on the subject, including the present authors, have assumed that the solid materials came down as fuel soot from partly burned gasoline.† A reanalysis of this condition, however, indicates that only very small amounts of fuel soot are likely to be available in equipment which produces large amounts of winter sludge; for instance, rubbish-collecting trucks which idle steadily during the greater part of an eight-hour trip covering 14–18 miles. Under these conditions the engine will be warm, even though the crankcase may be cool, and not much soot can be expected to form by chilled combustion. In a fleet operated under the authors' observation the collecting of water in the crankcases has been avoided by suitable control of temperature. However, the accumulating of carbonaceous material has continued, but only in proportion to the oil consumption of the individual engines. Units showing large amounts of solids in the crankcases and valve compartments invariably showed high oil consumption also. From this it seems more probable that the solid materials (which would serve as emulsifiers for winter sludge if water were present) came from the wash-down of partly coked oil and "carbon" deposits formed above the piston; the carrying medium is the oil returning to the crankcases under conditions of high oil consumption. This is according to the discussion of low-temperature ring-fouling given by the authors in the 1937 A.S.T.M. paper mentioned above.‡

* By courtesy of L. W. Vollmer, Gulf Research and Development Company.
† Gruse and Livingstone, A.S.T.M. Symposium on Lubrication, 1937, p. 1.
‡ *Loc. cit.*, p. 10.

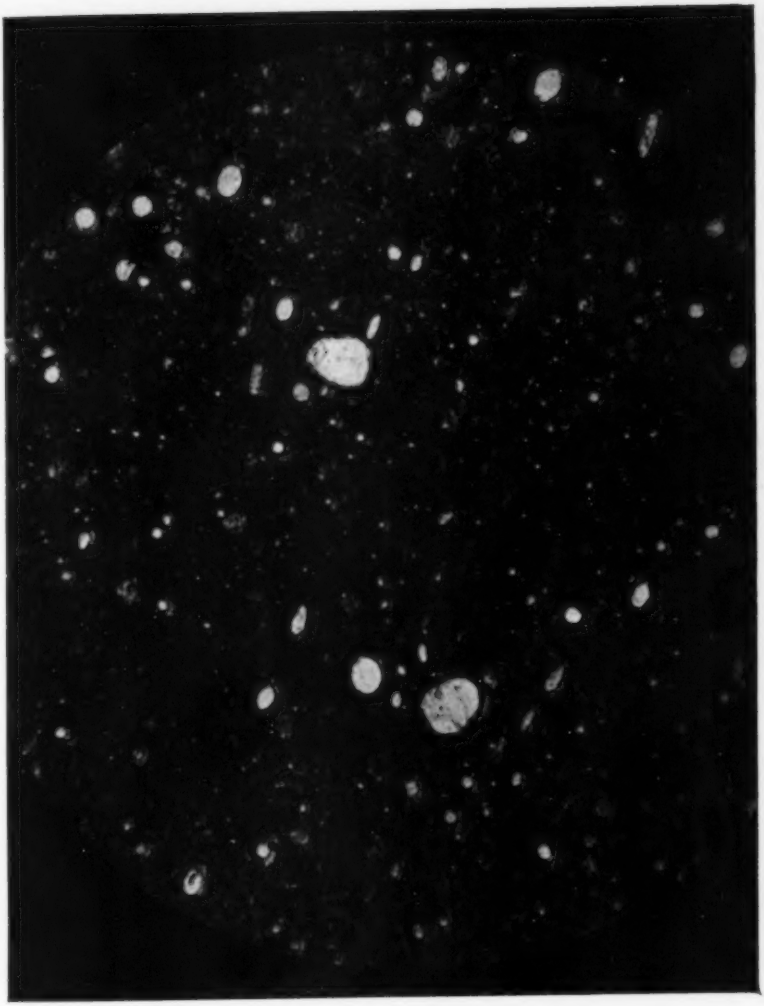

FIG. 2.

PHOTOMICROGRAPH (400 ×) OF WINTER SLUDGE.

[*To face p.* 424.

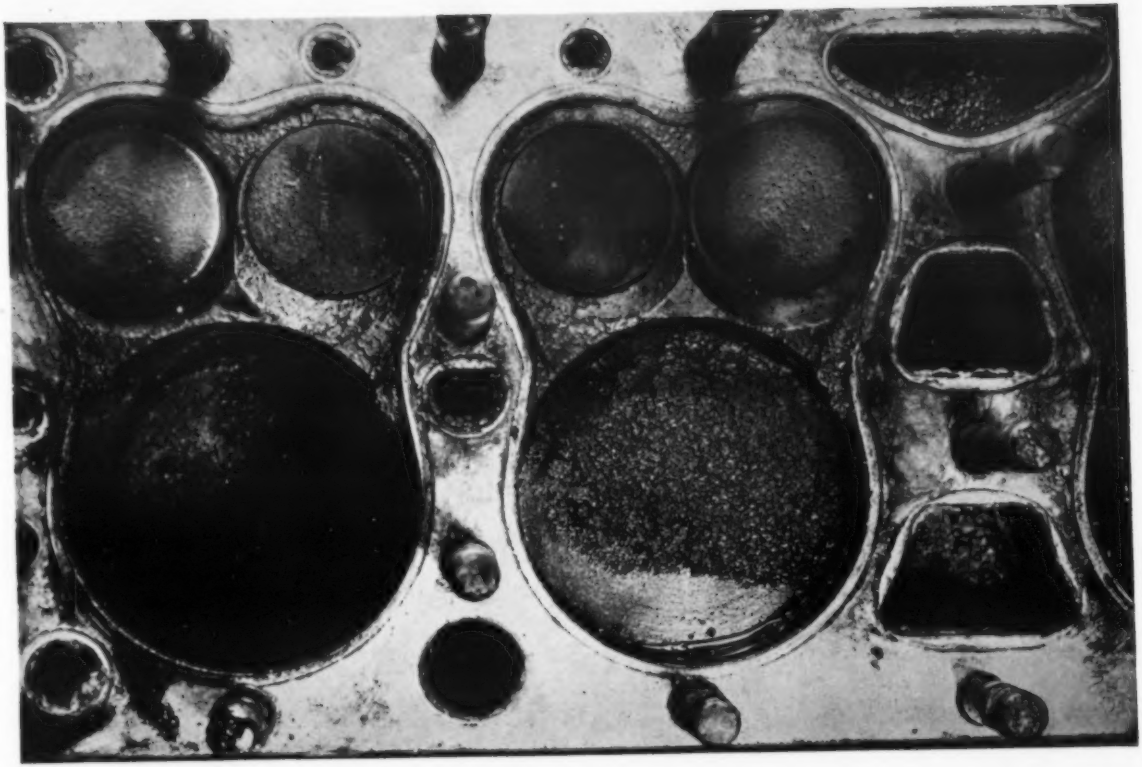

FIG. 3.

PHOTOGRAPH OF PISTON IN "V" TYPE ENGINE SHOWING OIL WASHING OF PISTON WITH HIGH OIL CONSUMPTION. A SMALL POOL OF OIL HAS FORMED AT THE LOWER EDGE OF THE PISTON.

PHOTOGRAPH OF PISTON IN "V" TYPE ENGINE SHOWING OIL WASHING OF PISTON WITH HIGH OIL CONSUMPTION. A SMALL POOL OF OIL HAS FORMED AT THE LOWER EDGE OF THE PISTON.

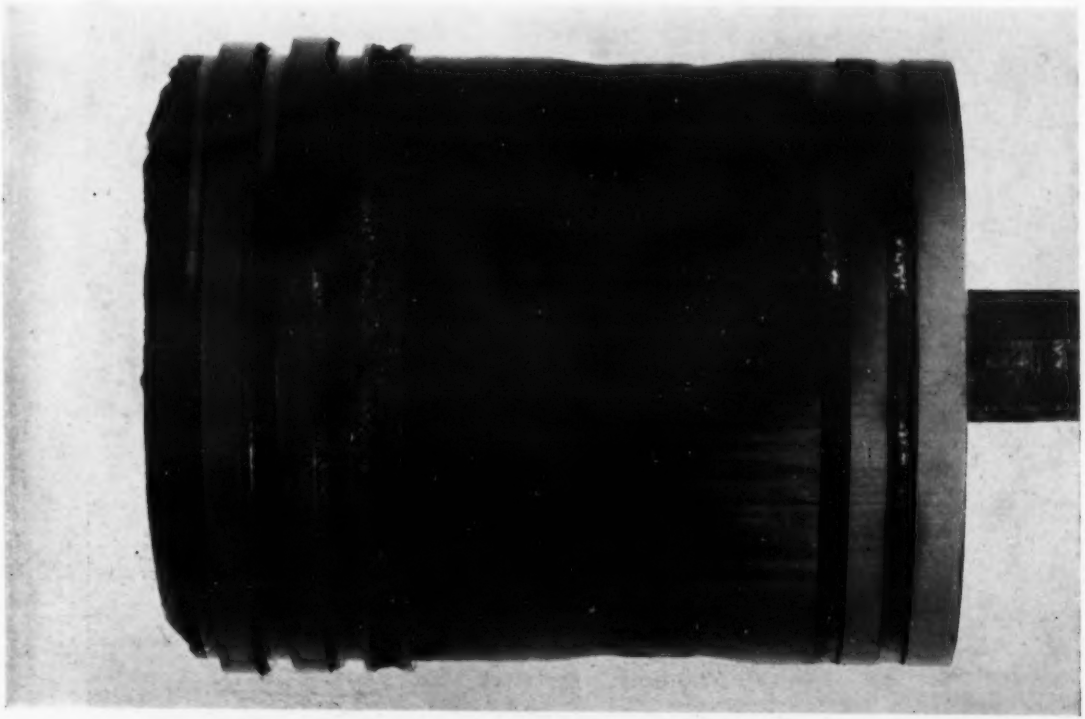

FIG. 5.

PHOTOGRAPH OF PISTON FROM EXPERIMENTAL ENGINE AFTER 40 HOURS OF OPERATION ON OIL B (SEE TEXT).

FIG. 6.

25 × ENLARGEMENT OF A SMALL CHIP TAKEN FROM A FEATHER EDGE AT THE TOP OF THE PISTON USED IN THE TEST WITH OIL C (SEE TEXT). ARROWS POINT TO AREAS SHOWING GLOBULAR FORMATION WHICH INDICATE THE DEPOSIT WAS MOLTEN WHEN HOT.

The operation of such a washing action is indicated in the accompanying photograph (Fig. 3). The normal deposit, which might be expected to form over the entire piston surface, has been washed away on the low side of the piston of a " *V* " type engine, leaving clean metal. A small pool of the washing oil can be seen at the edge of this piston. The combustion chamber deposits formed under conditions of low temperature and part load are well known to be of the soft and pasty variety. They are made up of 20–45 per cent. liquid oil, about 10 per cent. asphaltenes and resins, and the rest coke, lead and ash.* Such wet mixtures are easily extracted and disintegrated by hot oil. Hot unburned gasoline residues from starting, choked operation and running under very light load, will begin the process of washing this down off the piston crown into the ring grooves. Only very small particles can pass the rings, because of a combination of grinding and edge filtering. When the wash-down material reaches the oil ring-slots and piston drain-holes it has cooled somewhat, and apparently some of the resins come out of solution on the walls of the slots; this is indicated by inspection of oil rings which have been clogged. This resin layer then acts as an adhesive to bind solid particles from the disintegrated piston crown material. As pointed out in our 1937 paper, the build-up proceeds from the outside towards the inside of the slots. Experiments in our laboratory have led us to believe that the binder in the low-temperature carbon deposits resembles closely conventional oil varnish, and the ring clogging under discussion depends on a transfer of this binder from piston-crown to ring-groove slots. Since the slots and drain holes were originally provided to permit return of oil to the crankcase, the clogging of these passages interferes with the normal action of the oil control rings, and oil consumption increases. Once complete clogging has occurred it is practically impossible to clean the oil-control system in any way except by mechanical cleaning. If this explanation is correct, there is considerable danger that certain types of solvent " carbon removers " might be responsible for a good deal of ring-clogging trouble, since they may dissolve the carbon binder and wash it down the sides of the piston.

Once rings are clogged, oil consumption increases and the condition goes from bad to worse. The ring-clogging discussed above can be largely attributed to solvent and mechanical action exerted on deposits formed above the rings. There is, however, another set of causes and events which leads to the same result and which occurs under conditions of efficient high-temperature operation when the piston crown remains more or less clean. The starting-point for this sequence of engine trouble is the varnishing of the surfaces in the vicinity of the oil ring groove. In the course of our study of engine varnishes we encountered a series of results in which varnish deposit was not severe enough to cause piston-sticking, but did bring about a very marked increase of oil consumption. Two oils were compared: one was an S.A.E. 20 paraffinic oil with low resistance to sludging, and the other was an S.A.E. 30 naphthenic oil containing a

25 × ENLARGEMENT OF A SMALL CHIP TAKEN FROM A FEATHER EDGE AT THE TOP OF THE PISTON USED IN THE TEST WITH OIL C (SEE TEXT). ARROWS POINT TO AREAS SHOWING GLOBULAR FORMATION WHICH INDICATES THAT DEPOSIT WAS MOLTEN WHEN HOT.

* These figures are from deposits in experimental engines. Even short operation at higher temperature will dry the deposits, bringing them nearer to—

Liquid oil	10–20%
Asphaltenes and resins .	2–5
Coke, lead and ash . .	80–85

viscosity index improver. The inspection data on the two are given as follows:—

	Naphthenic blend.	Paraffinic oil.
Specific gravity . . .	0·8827	0·869
Viscosity at 100° F. . .	490	354
Viscosity at 210° F. . .	64·1	57·4
V.I.	102	110

When operated under identical test conditions of accelerated oxidation, the two oils gave results indicated in the accompanying Fig. 4. It will

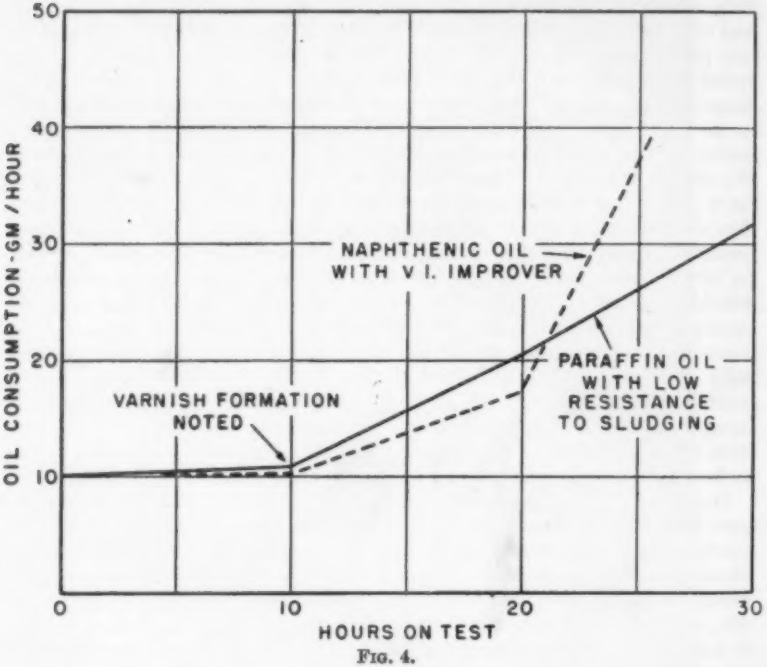

FIG. 4.

be observed that oil consumption stayed low to the point at which varnish deposition around the oil ring grooves was noted. Oil consumption then increased rapidly to the end of the test without any further marked indication of additional varnishing. Under comparable conditions, other oils showing high resistance to varnishing went through the entire test period without any increase of oil consumed per hour. No ring clogging was encountered in any of these latter cases because the engine was being operated with extremely high output; all oil passing the rings was burned cleanly in the combustion chamber. If a cycle of low load operations had been introduced at this point, oil-ring clogging would be expected to occur.

In order to study the sequence further, the work was transferred to another engine characterized by low crankcase temperature and absence of crankcase oxidation; the device was adopted of supplying oils pre-oxidized to different extents. An S.A.E. 40 solvent-refined naphthenic oil, preoxidized in an iron apparatus at 280° F. to the following test values, was employed :—

Neut. number . . .	0·54	Naph. insol. . . .	0·081%
Sapn. number . . .	5·7	Chloroform sol. from naph. insol.	0·027%

The results may be tabulated as follows :—

Hours on test.	Oil consumption, gm./hour.	Varnish around oil-ring groove.
20	2	Slight
40	3	No change
60	3·5	No change
80	3·5	No change

It is evident that no further varnishing and no increase in oil consumption occurred with long-extended running. The explanation apparently was that the supply of oxidation products contributing to varnish deposition had been exhausted during the first 20 hours of running. The test was repeated, but at the 40-hour period the crankcase was drained and a second filling of the same preoxidized oil was supplied. The results are as follows :—

Hours on test.	Oil consumption, gm./hour.	Varnish around oil-ring groove.
20	4·7	Slight.
40	4·8	No change.
	Oil changed; preoxidised oil again supplied.	
60	3·2	Heavy.
80	10·3	Ring slots partly clogged.
90	6·5 *	Ring clogged and stuck; cylinder scored.

* The decrease of oil consumption after 80 hours is striking and seems contradictory; however, it is believed to be due to the sharp increase of blow-by at this stage.

The inspection of the remaining crankcase oil showed no marked change from the values given above, except a 35 per cent. decrease of saponification number. Evidently in this case the saponifiable constituents served as a source for the varnish deposits.

This sequence was then repeated three times in a somewhat different way. A new base oil was used in each case, and 10 per cent. increments of a preoxidized oil were added to it at 20-hour intervals with inspections at each 10-hour point. The base oils were :—

(*a*) A highly refined paraffinic, S.A.E. 30,
(*b*) A solvent-extracted Mid-Continent, S.A.E. 30,
(*c*) A solvent-extracted naphthenic, S.A.E. 30,

respectively. The preoxidized material added was a solvent-refined Mid-Continent S.A.E. 10 oil, run in a test engine under high output and with crankcase oxidation at 280° F.; the oxidation run was carried to the point of varnish formation. The inspection data for this addition oil are as follows:—

Neut. number	4·4	Naph. insol.	0·902%
Sapn. number	23·1	Chloroform sol. from naph. insol.	0·808%

In all three cases the set of phenomena repeated itself, varnishing and oil-ring clogging occurring in turns, but in 40–50 hours instead of 80, presumably because the addition material had been more drastically oxidized. The accompanying Fig. 5 shows the piston from the B test (solvent-extracted Mid-Continent base oil) after 40 hours of running; the other pistons were almost exact duplicates. The heavy varnishing, the clogging of oil-ring slots, and the build-up of decomposed varnish around the compression ring grooves and the top edge of the piston are easily observed. The fact that the varnish material may be molten when deposited is indicated by the photomicrograph given in Fig. 6.* This is a 25× enlargement of a chip taken from a feather edge at the top of the piston used in the C run above. Typical indications of a molten condition are indicated by the arrows; the whole resembles to some extent a chilled lava or clinker of fusible material.

The inspection data on the used oils drained from the engine at the end of each test are as follows:—

	Oil A.	Oil B.	Oil C.
Viscosity at 100° F.	512	548	488
Neutralization number	0·57	0·58	0·66
Saponification number	4·5	5·3	4·8
Naphtha-insoluble, %	0·196	0·156	0·149
$CHCl_3$-soluble	0·139	0·121	0·092

These results are all of the same order of magnitude because the preoxidized oil added to each was in all three cases identical.

The entire set of data indicates that the phenomena are due to the decomposing of soluble oxidation products on hot surfaces. The various sources for varnish deposited on pistons, listed earlier in this paper, can presumably contribute equally to this form of varnishing, and thus cause serious interference with the functioning of the devices set up for control of oil consumption.

Conclusion.

The general effect of the work presented here is to indicate that engine-varnishing, ring-sticking, and oil-ring clogging are more or less closely related. Oxidation of the oil, chiefly in the crankcase, to unstable products, followed by the decomposing of these products at hot points in the engine, play an important part in all three.

* By courtesy of L. W. Vollmer, Gulf Research and Development Company.

It is recognized that increased outputs necessarily involve higher piston and cylinder-wall temperatures. However, it does not seem necessary that crankcase temperatures must also be higher. Since the effect of increased temperature on rate of oxidation is enormous—a 20° F. rise means approximately a doubling of the oxidation rate—every decrease in crankcase temperature means a real improvement. While it is true that the oil is exposed to more severe conditions for short time periods, it must be remembered that the bulk of the oil spends most of its time at the crankcase temperature. It seems reasonable, therefore, to hope that engine designers can arrange to keep crankcase oil temperatures low. They will thus take an unnecessary load off the oil, leaving it in better condition to carry the necessary load it encounters on the piston, cylinder walls, and bearing surfaces.*

* It is believed that these remarks apply to all oils, whether or not compounded, inhibited or otherwise altered by additive agents.

STUDIES ON THE SEPARATION OF PARAFFIN WAXES.* PART II—PHASE RELATIONSHIPS.

By M. F. Sawyer, Ph.D., A.M.Inst.Pet., T. G. Hunter, D.Sc., Ph.D., M.Inst.Pet., and A. W. Nash, M.Sc., F.Inst.Pet.

It has been mentioned in Part I that the only available method for the elucidation of the wax equilibrium diagram involves the separation and analysis of the solid and liquid equilibrium phases formed at temperatures within the melting range of the wax stock.

Apparatus for Equilibrium Experiments.

The apparatus used throughout these equilibrium experiments is illustrated in Fig. 1.

Constructed in brass, it consists essentially of three sections :—

(1) the cylinder *AB* of diameter 5 cm. and length 14 cm., which is screwed into

(2) the cylinder head *CD*, through which passes the screw *E* carrying the piston head *F*, and

(3) the conical cylinder head *G*.

The piston *F* consists of a brass plate with a rubber washer, the purpose of the latter being to prevent seepage of the liquid phase between the piston and the cylinder wall. The conical cylinder head *G* contains a perforated brass filter plate *HI* of diameter 4·7 cm. and thickness 4 mm., on which is placed a layer of thin canvas *L*, which, in turn, is covered with a layer of filter-paper. The liquid phase passing through the filter-plate was collected in a Buchner flask attached to the conical cylinder head by means of a rubber bung at *K*. All screw connections were made water-tight by the use of Mobilgrease Water-pump Grease No. 6.

Experimental Procedure.

The portion of the apparatus described under (1) and (2) above was assembled in an inverted position with the wheel handle pointing downwards, and placed in a thermostat of 10 gallons capacity. The thermostat was of the normal electrically controlled type, and the bath temperature was easily maintained to within $\pm 0{\cdot}05°$ C., an accuracy that was considered adequate for the purpose. The apparatus, which was maintained in the inverted vertical position by means of a cradle support attached to the inside of the bath, was allowed to attain the thermostat temperature, and the molten wax sample, normally of 70–80 grams, was then poured from a glass beaker into the cylindrical section of the apparatus. The liquid was stirred occasionally during the initial stages of cooling, but stirring was

* Paper received April 1940.

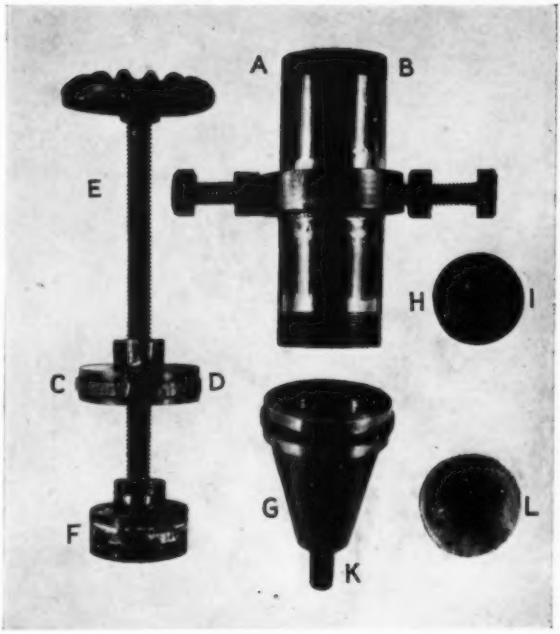

FIG. 1.

[*To face p.* 430.

almost continuous from the time solid wax first appeared until the liquid/solid wax mixture had cooled to the equilibrium or thermostat temperature. After reaching this temperature the mixture was allowed to stand for a further 6 hours, during which time stirring was intermittent. At the end of this period the conical cylinder head with Buchner flask attached was screwed into position at *AB*. The apparatus was then completely immersed in the thermostat and allowed to remain in this position for 1 hour, so that the whole apparatus attained the bath temperature. The apparatus was then momentarily taken from the thermostat, *inverted*, and immediately replaced in the cradle support which had been so designed that the whole

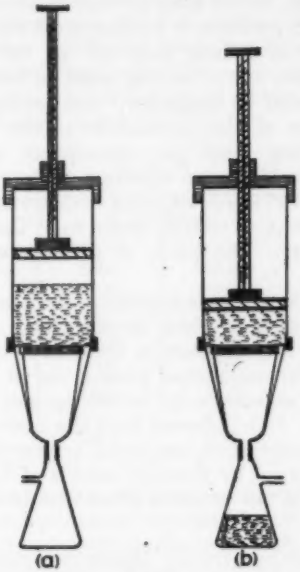

FIG. 2.

appartus (except for a portion of the screw *E*) was immersed whilst being supported in the position shown in Fig. 2.

Pressure was then applied to the solid/liquid equilibrium mixture by slowly turning the screw *E*. This procedure was continued until it was found impossible to turn the screw further. This operation was carried out over a period of 30–45 minutes, following which the apparatus was allowed to remain in the thermostat for a further period of 2 hours, the screw *E* being maintained in the position of maximum pressure. The apparatus was then taken from the thermostat, the Buchner flask containing the liquid phase removed from the conical cylinder head *G*, and the conical head separated from the cylinder by disconnecting at *AB*. The solid phase was removed from the cylinder as a solid block by turning the screw *E*. The amount of liquid phase was determined by weighing the Buchner

flask before and after the experiment. The melting point of each phase was found in the manner described later.

Fig. 2 illustrates respectively the set-up of the apparatus (*a*) immediately preceding the separation of the two phases, and (*b*) on completion of the separation.

Since pressure was employed to assist phase separation, the effect of such pressure on the solid–liquid equilibrium must be considered. This may be predicted by Le Chatelier's principle. When the pressure on a solid and liquid in equilibrium at the melting point is increased, the phase with the larger specific volume tends to disappear. In this case liquid paraffin wax has the greater specific volume, and pressure will cause some of the liquid to solidify, latent heat of solidification will be evolved, and the new equilibrium temperature or melting point will be higher.

Taking three waxes of melting point 65° C., 56° C., and 44·5° C. the specific volumes of which at the melting point in both the liquid and solid states have been reported by Carpenter,[1] and assuming their latent heats of fusion to be those of the *n*-paraffins of the same melting point,[2] the increase in melting point per atmosphere pressure increase has been calculated by the Clapeyron equation to be approximately + 0·01° C./atmosphere. Bunsen[3] has determined the increase in melting point with pressure of a paraffin wax of melting point 46·3° C. and reports a value of + 0·036° C./atmosphere. The effect of pressure on the equilibrium is obviously small.

During actual filtrations in this apparatus the pressure applied is small, but is increased considerably when the filter-cake is pressed to remove liquid. The effect of this pressure is two-fold: first to improve solid–liquid separation by the mechanical forcing out of liquid from the cake, and secondly to retard separation by solidifying part of the liquid wax still retained by the cake. It is believed that the first effect more than outweighs the second, since pressure was found to improve the separation, and as retention of liquid phase by the solid cake is of more importance in the equilibrium results than the pressure effect, the latter may be ignored in comparison.

Melting-point Determination.

The melting points were determined by the following method, for which only 5 grams of the sample were required. A $\frac{3}{4} \times 8$ inch glass test-tube was filled to a mark ($1\frac{1}{2}$ inches from bottom) with the wax sample and placed in an air-jacket consisting of a larger glass boiling tube ($1\frac{1}{2} \times 6$ inches), which, in turn, was placed in a 3-litre beaker containing water at a temperature 10–15° F. lower than the expected melting point of the sample. An N.P.L. Standardized I.P.T. Wax Setting-point Thermometer was placed in the molten sample so that the thermometer bulb reached to within $\frac{1}{4}$ inch of the bottom of the test-tube. A cooling curve was then plotted, the temperature being taken at half-minute intervals, starting at a temperature 5° F. above the melting point of the wax, and continuing until the first minumum cooling rate had been passed. The melting point was taken as that temperature at which five or more identical consecutive readings were observed. Taking all precautions mentioned in the I.P.T. method, Serial Designation-PS 11a, regarding the heating

of the sample, duplicate results are obtained differing by not more than $\pm 0{\cdot}05°$ F.

For the purposes of this research the melting point of paraffin wax is therefore defined as the temperature at which molten paraffin wax, when allowed to cool under the conditions specified above, first shows the minimum rate of temperature change. The values determined in this way will be referred to hereafter as I.P.T. melting points.

Experiments with De-oiled Slack Wax.

The first series of experiments designed to give some indication of the form or nature of the equilibrium diagram were made with a wax stock consisting of de-oiled slack wax of I.P.T. melting point 114·0° F. Equilibrium experiments were conducted over the temperature range 91·3°–108·7° F. in the manner described above. In each case the yields and I.P.T. melting points of the solid and liquid phases were determined, with the results shown in Table 1 below :—

Table I.

Experiment.	Equilibrium temperature, ° F.	% by Weight.		I.P.T. melting point.	
		Solid phase.	Liquid phase.	Solid phase, ° F.	Liquid phase, ° F.
1	91·3	89·1	10·9	117·2	91·0
2	96·1	78·2	21·8	119·3	96·0
3	97·9	75·6	24·4	119·8	97·7
4	99·6	72·1	27·9	120·0	99·3
5	103·4	58·1	41·9	122·5	103·2
6	104·5	54·5	45·5	123·0	104·3
7	108·7	33·2	66·8	125·7	108·6

These results are shown graphically in Fig. 3, which can be provisionally considered to represent equilibrium between the two phases formed by the wax stock at temperatures within its melting range.

In this figure the ordinate and abscissa represent equilibrium temperature and I.P.T. melting point respectively. The " liquidus curve " on the left was obtained by plotting the I.P.T. melting point of the separated liquid phase against the equilibrium temperature, whilst the " solidus curve " on the right was obtained by plotting the I.P.T. melting point of the separated solid phase against equilibrium temperature. This diagram represents graphically the experimentally determined phase relationships. In experiment 4, for example, the stock wax was maintained at a temperature of 99·6° F., indicated on the figure by point M^1.

The stock wax under these conditions M was separated into a liquid phase L of I.P.T. melting point L^1 equal to 99·3° F., and a solid phase S of I.P.T. melting point S^1 equal to 120° F. It is believed, however, that the experimentally prepared solid phases were not entirely free from liquid phase retained mechanically in the solid.

The complete removal of such entrained liquid phase is exceedingly difficult, and the actual phase separation obtained was the best possible

with the facilities available, and hence the diagram, while not representing true equilibrium, is the nearest possible approach to it. In true equilibrium the solidus curve would undoubtedly be displaced somewhat to the right of that in the figure.

If the equilibrium curve is analogous to that for a continuous series of solid solutions formed by two pure components as described in Part I, then the diagram should be applicable to a multi-stage removal of liquid at different temperatures. Thus, the solid phase of I.P.T. melting point 119·3° F. from experiment 2 (Table I), if allowed to attain equilibrium at a temperature of 104·5 F., should produce a solid phase of I.P.T. melting point 123·0° F., for in experiment 6 the equilibrium temperature of 104·5° F. produced a solid phase of this I.P.T. melting point. Accordingly, the solid phases resulting from experiments 1, 2, and 3 were in each case

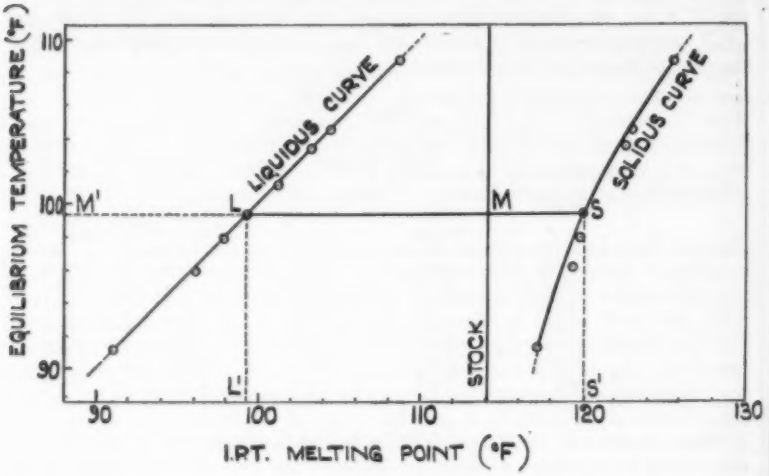

FIG. 3.

allowed to reach equilibrium at a higher temperature, after which the liquid phase was removed in the usual manner. The results of these three two-stage experiments are given in Table II (p. 435), under experiments 1(*a*), 2(*a*), and 3(*a*) respectively.

The results from each of these two-stage processes are summarized in Table III (p. 435), and also compared with the appropriate one-stage experiment.

It will be noted from Table III that a one-stage removal of liquid phase from the original stock at an equilibrium temperature of 103·4° F. resulted in a solid phase of I.P.T. melting point 122·5° F., whereas for a final equilibrium temperature of 103·5° F. in the two-stage process a solid of I.P.T. melting point 120·6° F. was obtained. Similar results are observed when the solid phases obtained in experiments 2(*a*) and 3(*a*) are compared with that obtained in a one-stage removal of liquid at the equilibrium temperature of 104·5° F.

TABLE II.

Experiment.	Expt. No.	Equilm. temp., ° F.	% by wt. Solid.	% by wt. Liquid.	I.P.T. M.Pt. Solid, ° F.	I.P.T. M.Pt. Liquid, ° F.
First Stage. Expt. 1. Table I . . .	1	91·3	89·1	10·9	117·2	91·0
Second Stage . .	1(*a*)	103·5	77·6	22·4	120·6	103·4
First Stage. Expt. 2. Table I . . .	2	96·1	78·2	21·8	119·3	96·0
Second Stage . .	2(*a*)	104·9	85·4	14·6	121·6	104·6
First Stage. Expt. 3. Table I . . .	3	97·9	75·6	24·4	119·8	97·7
Second Stage . .	3(*a*)	104·5	88·7	11·3	121·4	104·2

TABLE III.

Expt.	Equilibrium temp. ° F.	Solid Phase.	
		% by Weight.	I.P.T. Melting point, ° F.
1 and 1(*a*)	103·5*	69·0	120·6
5	103·4	58·1	122·5
2 and 2(*a*)	104·9*	66·8	121·6
6	104·5	54·5	123·0
3 and 3(*a*)	104·5*	67·0	121·4
6	104·5	54·5	123·0

* Equilibrium temperature of second stage.

It is apparent from these experiments that a two-stage process results in a solid phase of lower I.P.T. melting point than that obtained in a one-stage experiment on the original stock at the higher of the two equilibrium temperatures. The results of the three two-stage experiments are illustrated in Fig. 4, in which *AB* is the solidus curve of Fig. 3. It would appear that an equilibrium diagram similar to that shown in Fig. 3 applies only to a one-stage fractional melting process, and that it is not applicable to a multi-stage fractional melting process for the separation of paraffin waxes.

The fact that the solid phase obtained in the second stage of a two-stage process does not fall on the " solidus curve " of the equilibrium diagram could be explained by the incomplete separation of the liquid and solid phases, some liquid phase being retained by the solid phase, and hence lowering its I.P.T. melting point. Assuming that I.P.T. melting point follows the mixture rule, the amount of liquid phase retained in this way by each two-stage solid may be estimated. Thus, it has been calculated

that a 10 per cent. retention of liquid (expressed as a percentage of the solid phase) would account for the difference in I.P.T. melting point between the one-stage and two-stage solid phases obtained at the same equilibrium temperature in experiments 1(*a*), 2(*a*), and 3(*a*). In these three experiments the phase separations were all carried out in a similar manner at nearly constant temperature (103·5–104·5° F.). Equilibrium experiments conducted in the same equipment at a constant temperature of 81° F. in which the solid and liquid phases were wax and a solution of wax in toluene respectively indicated that the percentage retention of liquid by solid phase

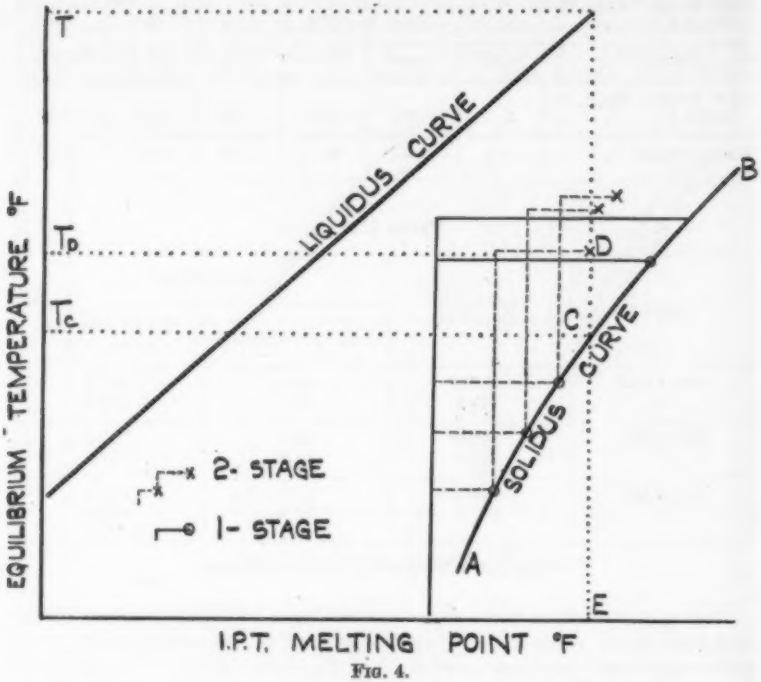

FIG. 4.

was, as shown in Fig. 5, a function of the ratio solid phase/liquid phase. It will be seen from this figure that for the same solid/liquid ratios as those prevailing in experiments 1(*a*) to 3(*a*), viz. 3·5, 5·9 and 7·9 respectively, the percentage retention is nearly constant, as was the case with the calculated values for these experiments. The actual percentage retentions are not, of course, comparable, owing to the differences in the liquid phases. This would suggest that retention of liquid phase by solid phase could account for the difference between the one-stage and multi-stage "solidus curves."

Another explanation of the observed phenomenon is possible. In Fig. 4 the two waxes *C* and *D* have the same I.P.T. melting point—namely, *E*. On heating, wax *C* begins to melt at temperature T_C, whilst wax *D*

commences melting at the higher temperature T_D. Both waxes are completely molten at temperature T. Although both waxes have the same I.P.T. melting point, they have different melting ranges, wax C melting over the range $(T_C - T)$ and wax D over the range $(T_D - T)$, and hence different compositions. Even if the stock wax consisted simply of some half dozen n-paraffins, it is obvious that, completely independent of liquid phase retention, two solids could be obtained from it having the same I.P.T. melting point, but of different composition, and of course different

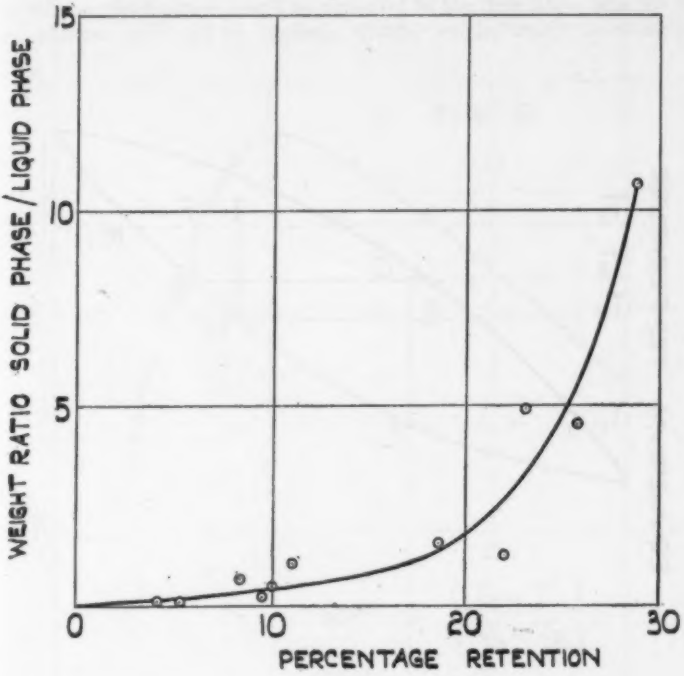

FIG. 5.

melting ranges. It is conceivable that a very large number of solid phases having identical I.P.T. melting points but different compositions could be obtained from even such a simple stock. Indeed, it is obviously possible, as was explained in Part I, to obtain a very large number of solid phases of identical molecular weight, or of identical melting point, density or other physical property, but differing compositions. In fact, the only satisfactory diagram for representing equilibrium in a system of n components is one showing n-1 composition variables or n-1 physical property variables. The major reason for the lack of coincidence of the one- and two-stage solidus curves is probably to be found in the method of representation, where the phases of a multi-component system are inadequately characterized in

terms of a single physical property variable, with retention of liquid phase by solid phase as an additional complication.

The "Sweating" Process of Fractional Melting.

An equilibrium diagram of the continuous solid solution type applying to the pure substances A and B is illustrated in Fig. 6. Consider a mixture

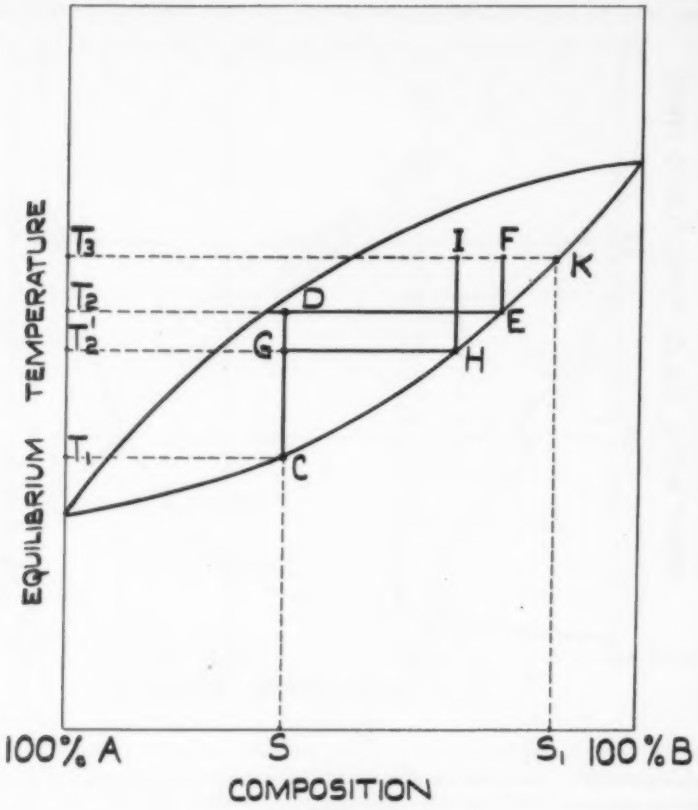

Fig. 6.

of A and B of composition S from which a solid of composition S_1 is to be prepared, by two-stage fractional melting over the temperature range T_1 to T_3.

The two-stage process may be carried out in two ways. First the temperature of the stock may be raised from T_1 to T_2, and after attaining equilibrium, the liquid phase is separated, then the temperature of the solid phase E may be raised to T_3 and the equilibrium liquid phase separated,

as illustrated by the steps *C D E F K*, where the temperature rise T_1 to T_2 is not equal to the temperature rise T_2 to T_3—that is, two stages of unequal temperature increments have been employed. In the second method, illustrated by the steps *C G H I K*, the two temperature rises T_1 to T_2' and T_2' to T_3 are equal. That is, two stages of equal temperature increments have been employed. It is obvious, of course, that the two stages of unequal temperature increments can be carried out in a very large number of different ways. The first-stage temperature increment must, of course, be smaller than the melting range of the original stock, otherwise no solid phase would be obtained in the first stage, and the two-stage process could not be applied. Similar results would be obtained if

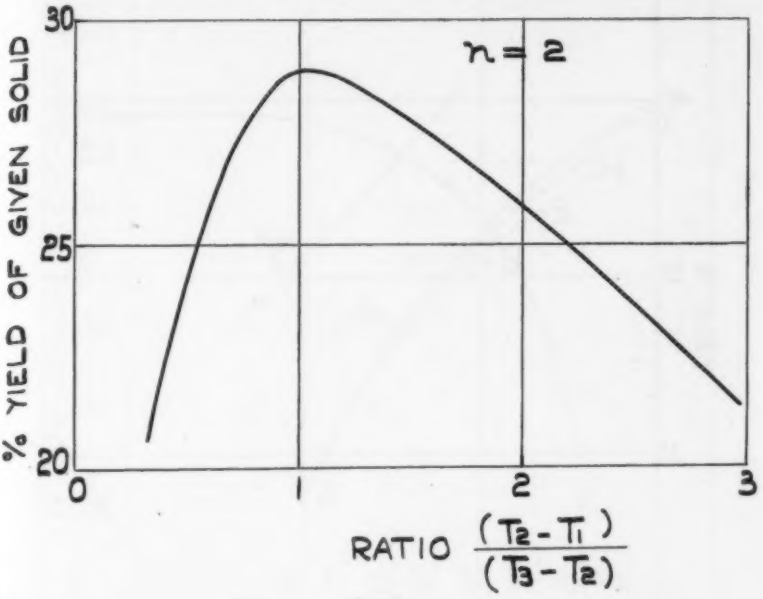

FIG. 7.

the second-stage temperature was greater than the melting range of the solid from the first stage. The temperature increment applied to the nth stage must therefore always be smaller than the melting range of the solid phase obtained from the $(n\text{-}1)^{th}$ stage.

In Fig. 7 the yield of a given solid obtained by some of these two-stage processes has been plotted against the ratio $(T_2-T_1)/(T_3-T_2)$, from which it will be observed that the yield is a maximum when the ratio $(T_2-T_1)/(T_3-T_2) = 1$—that is, when two stages of equal temperature increments are employed. This is a general rule, and the yield of a given solid for an n-stage process is a maximum when the stages are of equal temperature increments. This particular case is analogous to the multiple extraction of a solution with a liquid for which it has been proved that the

most efficient extraction is obtained when the solvent is subdivided into batches of equal volume.[5]

In Fig. 8 the yield of a solid of given composition is plotted against the number of stages n for an n-stage process, employing stages of equal temperature increments, from which it will be seen that the yield of a given solid approaches a maximum when n approaches infinity, but that this maximum yield is closely approximated in a finite number of stages—viz. 12

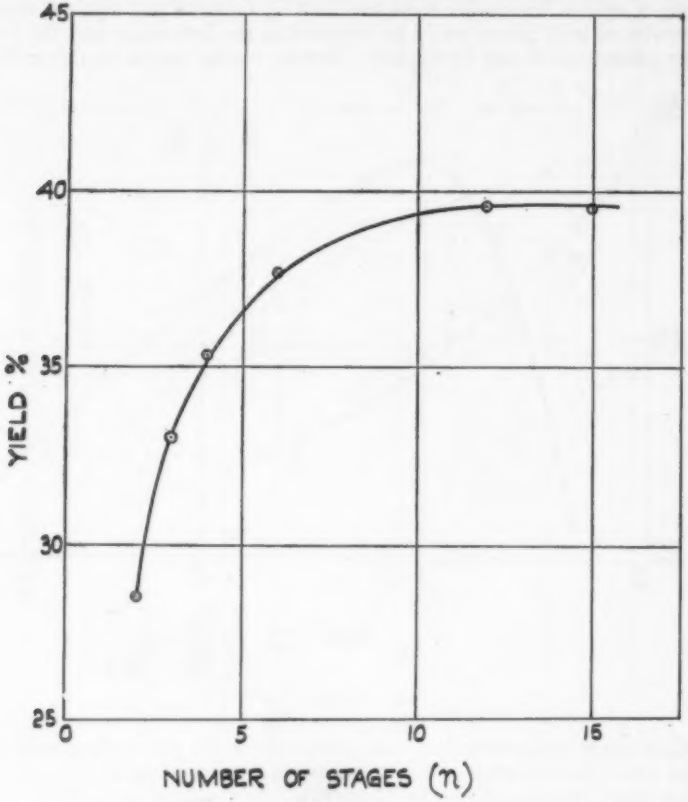

FIG. 8.

in the figure. Again an analogy exists between this and the multiple solvent extraction process, as the results obtained with a finite volume of solvent subdivided into a comparatively small finite number of batches approach those obtained with a finite volume of solvent subdivided into an infinite number of batches.[6]

In the "sweating" process of fractional melting, a mass of solid wax is subjected to a gradually increasing temperature over a period of some hours, with continuous removal by natural drainage of any liquid phase

formed, this operation being continued until solid wax of the required melting point remains.

If in such a "sweating" process the temperature is increased at a constant rate and the liquid phase is removed as it is formed, then this process will correspond to an infinite stage process of equal temperature increments. In actual practice, however, the complete removal of the liquid phase will not occur at the formation temperature, and, owing to such drainage lag combined with non-uniform heating, a lower yield than that from the above defined infinite stage or ideal process can be normally

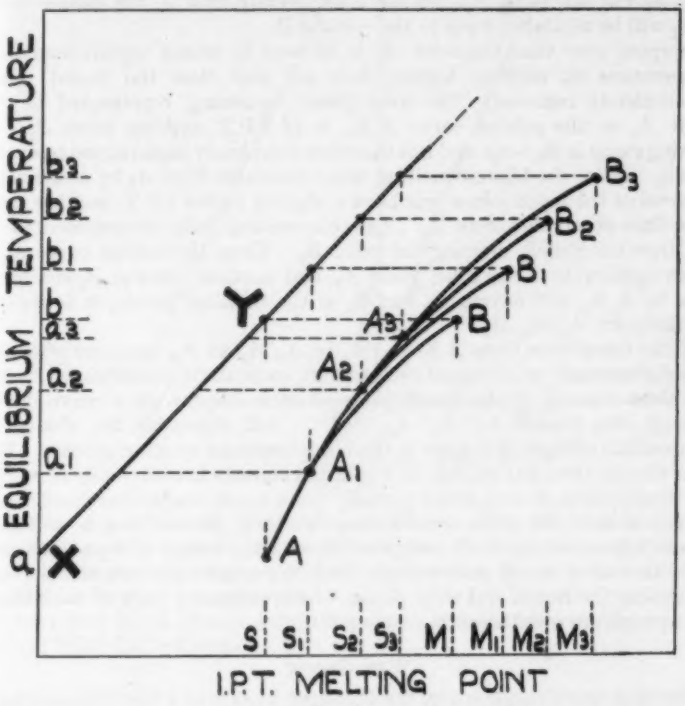

FIG. 9.

expected. An infinite stage process of equal temperature increments could therefore be used as a basis for computing sweating efficiency.

In Fig. 9 AB and XY are the solidus and liquidus curves applicable to equilibrium experiments involving a one-stage removal of liquid phase from a wax stock of I.P.T. melting point S and of melting range (b—a). The stock is completely liquid at the temperature b, and M corresponding to B, therefore represents the I.P.T. melting point of the highest-melting wax (solid phase) obtainable from this stock in a one-stage equilibrium experiment.

Suppose that the stock has attained equilibrium at a temperature a_1 slightly higher than a, and that the resulting liquid phase has been completely removed from the solid. The solid phase remaining, represented by point

A_1 on the solidus curve AB, will have a melting point of S_1. Now this solid phase has a melting range of $(b_1—a_1)$, and will be completely liquid at temperature b_1. Also, the highest-melting wax obtainable in a one-stage removal of liquid phase from the solid phase represented by A_1 will have an I.P.T. melting point slightly higher than M. Let this I.P.T. melting point be represented by M_1. The point B_1 is therefore defined in reference to temperature b_1 and I.P.T. melting point M_1. It is now clear that the solidus curve AB will apply to the original wax stock *only* and that another curve having A_1 and B_1 as terminal points is necessary for the solid phase A_1. As the new stock A_1 does not differ greatly from A, the solidus curve A_1B_1 will be similar in form to the curve AB.

Suppose now that the solid A_1 is allowed to attain equilibrium at a temperature a_2 slightly higher than a_1, and that the liquid phase is completely removed. The solid phase remaining, represented by the point A_2 on the solidus curve A_1B_1, is of I.P.T. melting point S_2; its melting range is $(b_2—a_2)$, and it is therefore completely liquid at the temperature b_2. Also, the highest-melting wax obtainable from A_2 by a one-stage removal of the liquid phase will have a slightly higher I.P.T. melting point than that obtainable from A_1. Let this melting point be represented by M_2, thus completely defining the point B_2. Thus, the solidus curve A_1B_1 is not applicable to the solid phase A_2, and another curve A_2B_2 similar in form to A_1B_1, and having A_2 and B_2 as the terminal points, is necessary. Similarly for A_3, A_4, A_5. . . .

If the transitions from A to A_1, A_1 to A_2, A_2 to A_3, etc., are obtained by infinitesimally small equal temperature increments accompanied by the complete removal of the liquid phase at each stage, then a curve drawn through the points A_1, A_2, A_3, A_4 . . . will represent the change in composition of the solid phase in the ideal fractional melting process. It is clear that as the ideal process of separation consists in completely removing the liquid phase at each infinitesimally small equal temperature increment, an approach to the curve representing this ideal process may be obtained by actually removing the liquid phase in as many stages of equal temperature increment as is conveniently and experimentally practicable, and subjecting the liquid and solid phases to the necessary tests at each stage. This procedure was therefore adopted.

Wax Stock.

The wax stock employed in the following work was a blend consisting of equal weights of four completely refined Iranian waxes of the following I.P.T. melting points: 130·95°, 127·85°, 119·85°, and 108·35° F. The resulting blend was of I.P.T. melting point 122·1° F.

Construction of the Fractional Melting-process Diagram.

Two series of experiments are necessary for the construction of the required diagram :—

(*a*) the determination of the solid/liquid curves representing a one-stage melting process, and

(*b*) the determination of the solid/liquid curves representing a multi-stage melting process. Actually a 14-stage process was employed, as has been shown in Fig. 8, the results from a twelve stage

process approach closely to those obtained from an infinite stage process for two substances giving an equilibrium diagram of the continuous solid solution type.

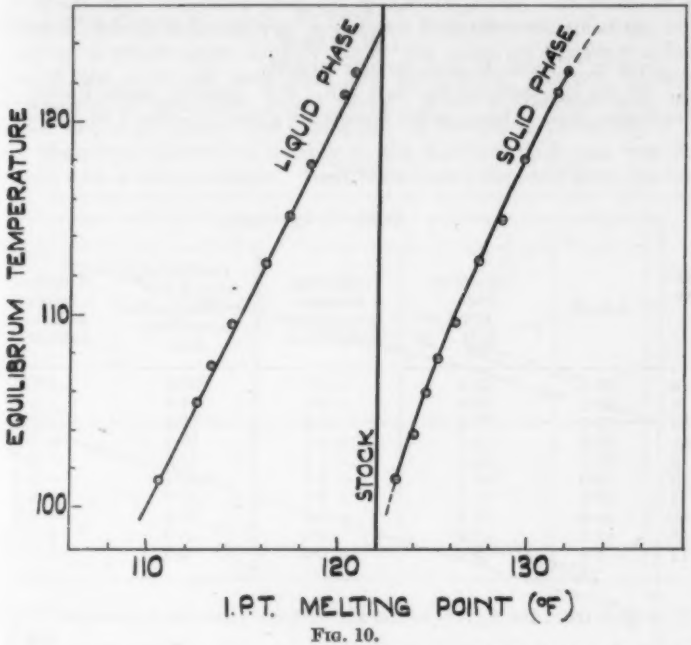

FIG. 10.

(*a*) *One-stage Removal of the Liquid Phase.*—The solid/liquid curves representing this process were determined at various temperatures covering the melting range of the wax stock using the procedure already described. In each experiment the yields and I.P.T. melting points of the solid and liquid phases were determined, and the relevant figures are given in Table IV as follows :—

TABLE IV.

Expt. No.	Equilm. temp. ° F.	% by weight.		I.P.T. melting point.	
		Solid phase.	Liquid phase.	Solid phase, ° F.	Liquid phase, ° F.
8	110·8	92·1	7·9	123·1	110·6
9	112·8	82·1	17·9	123·9	112·55
10	113·0	77·4	22·6	124·7	112·65
11	113·8	72·8	27·2	125·15	113·45
12	114·9	61·1	38·9	126·25	114·55
13	116·4	52·0	48·0	127·3	116·15
14	117·6	40·9	59·1	128·6	117·35
15	119·0	30·4	69·6	129·65	118·65
16	120·8	13·3	86·7	131·55	120·5
17	121·4	8·6	91·4	131·95	121·05

The results are shown graphically in Fig. 10.

The yield of solid phase was calculated from the I.P.T. melting points of the solid and liquid phases obtained in each experiment :—

(*a*) using the relation $T = \frac{414{\cdot}5\ M}{M + 94{\cdot}4}$, where T is the I.P.T. melting point in °F. and M is molecular weight.

(*b*) on the assumption that the I.P.T. melting point follows the mixture rule. Comparative figures are given in Table V as follows :—

TABLE V.

Expt. No.	Yield—% by weight.				
	Actual.	Calculated from $T = \frac{414{\cdot}5\ M}{94{\cdot}4 + M}$	Difference between actual and calculated.	Calculated from I.P.T. melting-point-by-mixture rule.	Difference between actual and calculated.
8	92·1	91·4	+ 0·7	92·0	+ 0·1
9	82·1	83·0	− 0·9	84·1	− 2·0
10	77·4	77·4	0·0	78·4	− 1·0
11	72·8	72·7	+ 0·1	73·9	− 1·1
12	61·1	62·4	− 1·3	64·5	− 3·4
13	52·0	51·1	+ 0·9	53·4	− 1·4
14	40·9	40·4	+ 0·5	42·2	− 1·3
15	30·4	29·8	+ 0·6	31·4	− 1·0
16	13·3	13·3	0·0	14·5	− 1·2
17	8·6	9·1	− 0·5	9·6	− 1·0

It is clear from the figures in the above table that the agreement between the actual and calculated yields is closer when the relation $T = \frac{414{\cdot}5\ M}{94{\cdot}4 + M}$ instead of the simple mixture rule is used for the calculation of the latter.

The yield/melting point graph for the two phases is given in Fig. 11, from which it is seen that the yield is a linear function of the I.P.T. melting point. For yields of the liquid phase lower than 10 per cent. the I.P.T. melting point is slightly lower than indicated by the linear relationship, and it is suggested that this may be due to the presence in the wax stock, of a small amount of oil, probably contained initially in the wax of I.P.T. melting point 108·35° F., the lowest melting of the four commercial waxes comprising the stock. Assume, for example, that the original 108·35° F. I.P.T. melting point wax contains 1 per cent. oil. The oil content of the wax stock, which contains 25 per cent. of this particular wax, is therefore 0·25 per cent. Now, it is likely that whatever the yield of liquid phase, most of the oil would be present in this phase, due to the press method employed for the separation of the phases. Thus, liquid phase obtained from an experiment in 5 per cent. yield would contain approximately 5 per cent. oil. By comparison with data obtained in determinations made to study the effect of the addition of oil on the I.P.T. melting point of a wax, it was concluded that the presence of this amount of oil would explain this deviation from the linear relation. With higher yields of liquid phase,

the oil/wax ratio decreases and the effect of the oil on the I.P.T. melting point becomes less pronounced until at 20 per cent. yield it is negligible, and the linear relationship then holds.

(*b*) *Multi-stage* (14-*stage*) *Removal of Liquid Phase.*—98 grams of the wax stock were placed in the apparatus and allowed to attain equilibrium at a temperature slightly above the point of complete solidification of the wax and such that the equilibrium mixture contained approximately 5 per cent. liquid phase. After equilibrium had been attained the experiment was completed as described previously. The liquid phase was allowed to solidify in the Buchner flask and was then removed with a nickel spatula. Last traces were removed from the flask

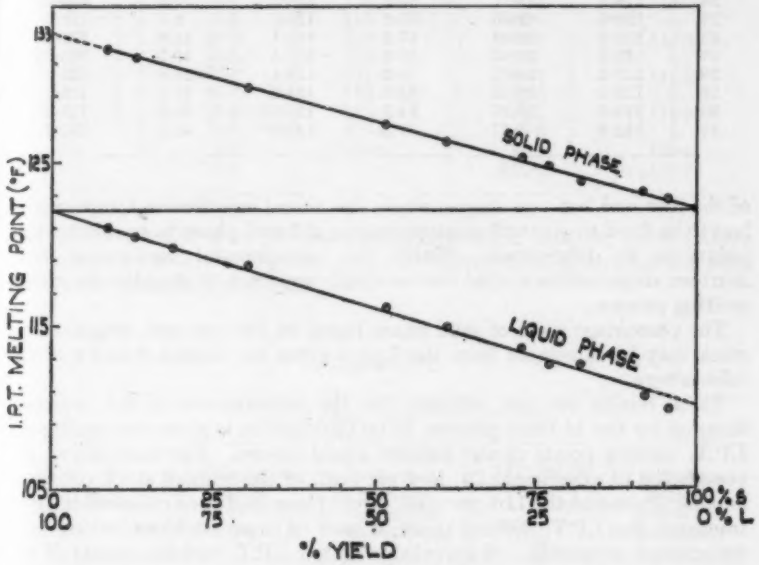

FIG. 11.

with petroleum ether; the solvent was evaporated and the traces of wax remaining were added to the bulk of the liquid phase. The solid phase was removed from the apparatus, weighed, its melting point determined, liquefied, and replaced in the apparatus. The thermostat was then set at a slightly higher temperature, such that approximately 10 per cent. liquid was present in the equilibrium mixture. After reaching equilibrium, the solid and liquid phases were separated in the usual manner and treated as described above. This procedure was repeated employing as nearly as possible equal temperature increments, until the quantity of solid remaining became so small that it was impossible to continue further. In all, fourteen separations were made. Essential figures for each of the fourteen experiments are given in Table VI. As far as possible equal temperature increments were employed in each succeeding stage, with the exception

TABLE VI.

Expt. No.	Equilm. temp. ° F.	Wt. solid phase taken gms.	Solid phase.		Liquid phase.	
			Wt. %.	I.P.T. melting point, ° F.	Wt. %.	I.P.T. melting point, ° F.
18	110·2	97·95	95·6	122·75	4·4	109·85
19	111·0	92·27	97·4	123·05	2·6	—
20	112·7	88·68	94·9	123·5	5·1	112·55
21	114·1	82·23	87·0	124·85	13·0	113·85
22	115·8	70·42	87·8	126·05	12·2	115·5
23	117·1	60·58	89·9	126·95	10·1	116·9
24	118·7	52·11	87·7	128·2	12·3	118·45
25	120·0	43·66	90·5	129·1	9·5	119·7
26	121·5	38·68	87·2	130·1	12·8	121·25
27	123·5	32·85	80·3	131·5	19·7	123·25
28	125·2	25·71	78·2	133·1	21·8	124·9
29	126·7	17·53	82·5	134·2	17·5	126·5
30	128·9	13·87	64·2	136·35	35·8	128·6
31	132·4	8·67	57·2	138·6	42·8	132·1

of the first and last two stages, where the actual equilibrium temperatures had to be fixed to give sufficient quantities of liquid phase to enable melting points to be determined. Within the experimental limitations these fourteen stage results are the best available approach to the ideal fractional melting process.

The percentage yield of solid phase based on 100 per cent. original wax stock may be calculated from the figures given in columns 3 and 4 of the table above.

These results are not sufficient for the construction of the complete diagram for the 14-stage process, as no information is given concerning the I.P.T. melting points of the blended liquid phases. For example, at the completion of experiment 20, 88·4 per cent. of the original stock remained as solid phase and the 11·6 per cent. liquid phase had been removed in three fractions, the I.P.T. melting point of each of these fractions having been determined *separately*. A knowledge of the I.P.T. melting points of the blended liquid fractions is desirable, and the fractions were therefore re-blended in their equivalent amounts and the I.P.T. melting point of each blend determined. Results are appended in Column 5 of Table VII (p. 447), in which are also recorded the yield of the solid and liquid phases as percentages of the stock.

The I.P.T melting point of the 100 per cent. blended liquid phase should, of course, be 122·1° F.—that of the original wax stock—and considering the number of steps involved in its determination, the actual figure of 121·95° F. obtained for the re-blended stock is very satisfactory.

As the yields of both phases and the I.P.T. melting point of the solid phase are known, the I.P.T. melting points of the various blended liquid phases may be calculated by applying the relation $T = \frac{414{\cdot}5\,M}{94{\cdot}4 + M}$. As a further test of the applicability of this relation, the yields of the phases were calculated in this manner from the known I.P.T. melting points.

TABLE VII.

Expt. No.	Solid phase.		Blended liquid phase.	
	Yield wt. % on stock.	I.P.T. melting point, °F.	Yield wt. % on stock.	I.P.T. melting point, °F.
—	100·0	122·1	0·0	—
18	95·6	122·75	4·4	109·85
19	93·1	123·05	6·9	110·25
20	88·4	123·5	11·6	—
21	76·9	124·85	23·1	112·55
22	67·5	126·05	32·5	—
23	60·7	126·95	39·3	114·05
24	53·3	128·1	46·7	—
25	48·2	129·1	51·8	115·30
26	42·1	130·1	57·9	—
27	33·8	131·5	66·2	116·95
28	26·4	133·05	73·6	—
29	21·8	134·2	78·2	118·35
30	14·0	136·35	86·0	—
31	8·0	138·6	92·0	120·4
—	0·0	—	100·0	121·95

The yields calculated on the assumption that I.P.T. melting point follows the mixture rule are also given, and the comparative figures for the solid phases are given in Table VIII :—

TABLE VIII.

Stage no.	Solid Phase, Yield % by Weight.				
	Actual.	Calculated from $T = \frac{414{\cdot}5\,M}{94{\cdot}4 + M}$.	Difference between actual and calculated.	Calculated from Melting-point-by-mixture rule.	Difference between actual and calculated.
4	76·9	76·5	+ 0·4	77·6	− 0·7
6	60·7	60·7	± 0·0	62·4	− 1·7
8	48·2	48·0	+ 0·2	49·3	− 1·1
10	33·8	34·1	− 0·3	35·4	− 1·6
12	21·8	23·3	− 1·5	23·6	− 1·8
14	8·0	8·6	− 0·6	9·3	− 1·3

It is clear from the data included in Tables V and VIII that agreement between the actual and calculated yields is closer when the relation $T = \frac{414{\cdot}5\,M}{94{\cdot}4 + M}$ is used for the calculation of the latter. The use of this relation is therefore justified for this wax stock, but at the same time it will be noticed that there is no very serious discrepancy between the actual and the calculated values when the latter are calculated on the assumption that the I.P.T. melting point follows the mixture rule.

Liquid/Solid Curves for Fourteen-stage Process.

The curves plotted from the data contained in Tables VI and VII are shown in Fig. 12.

The yield/I.P.T. melting point curves for the fourteen-stage process and also the corresponding curves for the one-stage process are given in Fig. 13. Comparison of the two curves for the respective solid phases confirms the conclusion already discussed that the yield of solid of any given I.P.T. melting point, within the range possible, is higher in a multi-stage than in a one-stage process.

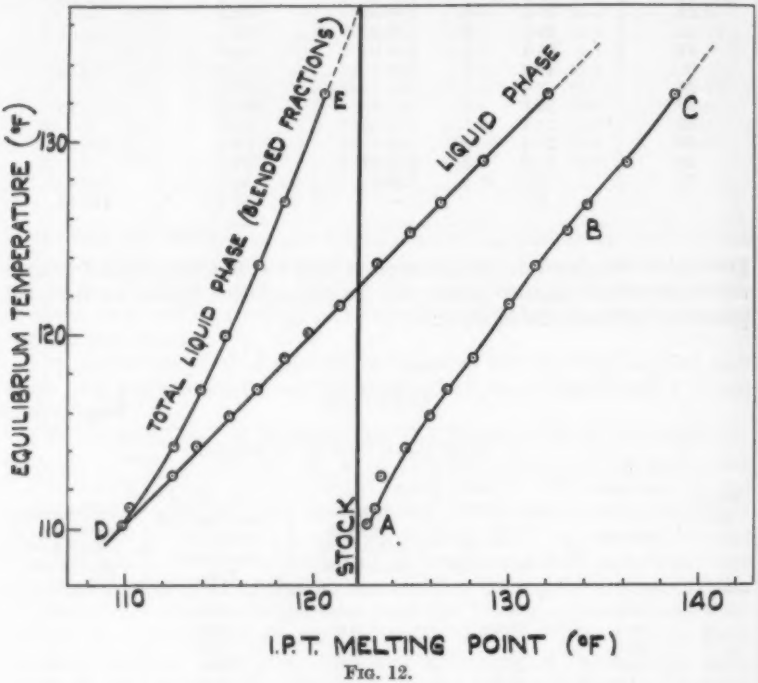

Fig. 12.

The complete diagram, which is applicable to the process both qualitatively and quantitatively, is given in Fig. 14, and is based essentially on Figs. 10 and 12, and includes the curve $T = \frac{414{\cdot}5\,M}{M + 94{\cdot}4}$. This diagram will be considered sectionally.

Curves *AB* and *DE*.

AB and *DE* represent the solidus and liquidus curves applicable to a one-stage separation of the two phases at any temperature within the limits of their co-existence. *AH* is the stock line, the wax stock having an

I.P.T. melting point of S' corresponding to a calculated molecular weight of S''. The temperature a corresponding to A represents the point at which the stock just begins to melt when heated. It is completely liquid at temperature b corresponding to B, and the temperature range $(b - a)$ therefore represents the melting range of the stock. It is found experimentally that the liquid phase has, in general, an I.P.T. melting point of 0·2–0·3° F. lower than the equilibrium temperature. The liquidus curve DE may therefore be considered as a straight line only slightly removed from the 45° line.

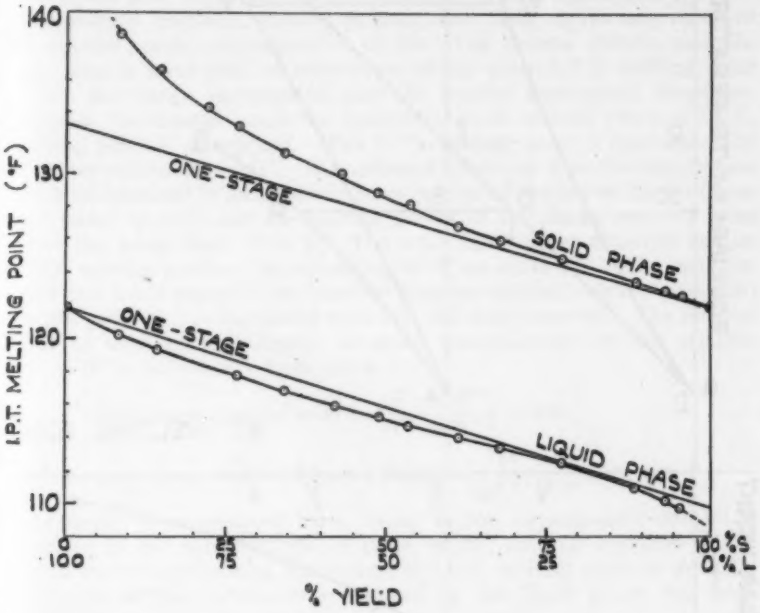

FIG. 13.

These curves may be applied quantitatively in the following manner. Suppose the stock attains equilibrium at any temperature x within its melting range, as represented by point S_1. The equilibrium mixture consists of solid and liquid phases represented respectively by the points P and Q on the solidus and liquidus curves, and having melting points of p' and q' and calculated molecular weights of p'' and q'' respectively. The relative amounts of solid and liquid phases at this temperature are calculated from the ratio $(S'' - q'')/(p'' - S'')$, from which

$$\text{percentage yield of solid phase} = \left(\frac{S'' - q''}{p'' - Q''}\right) \times 100$$

and

$$\text{percentage yield of liquid phase} = \left(\frac{p'' - S''}{p'' - q''}\right) \times 100$$

CURVES *AC*, *DEF*, AND *DG*.

The curves *AC*, *DEF*, and *DG* approach the infinite-stage or ideal fractional melting process curves. Curve *AC* represents the change in I.P.T. melting point of the solid phase during fourteen small approximately

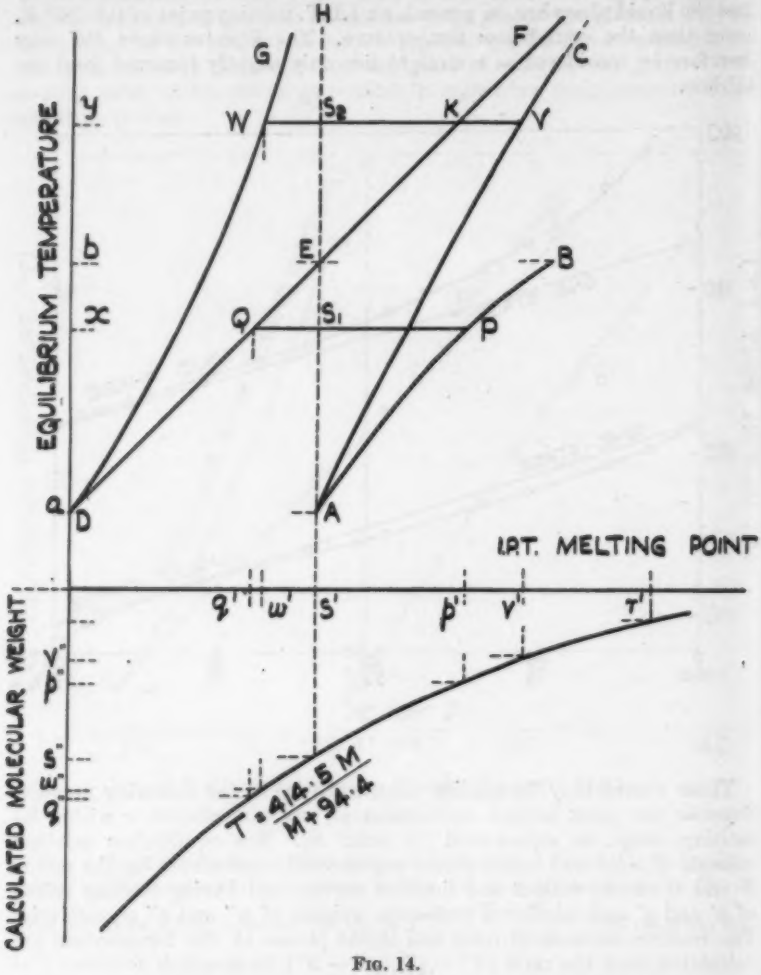

FIG. 14.

equal temperature increments, after each of which the resulting small amount of liquid phase is completely removed from the solid. It was found in the fourteen-stage experiments, as in the single-stage experiments, that the I.P.T. melting point of the liquid phase at each removal stage was, in general, 0·2–0·3° F. lower than the equilibrium temperature. The change

in I.P.T. melting point of the liquid phase is represented by *DEF*, where *DEF* may be considered, within experimental error, as a straight line. The composition of the blended liquid phases is given by the curve *DG*, and this curve therefore gives the I.P.T. melting point of the total blended liquid phase corresponding to any solid phase represented on *AC*.

It is clear that the solid phase changes in I.P.T. melting point along *AC*; the total liquid phase removed changes in I.P.T. melting point along *DG*; whilst the I.P.T. melting point of the liquid phase being removed at any stage of the process is given by the equivalent point on the curve *DEF*.

If as has been suggested this fourteen-stage process approaches the ideal infinite-stage fractional melting process, then these curves may be taken as approximately representative of the ideal process curves, and the approximate ideal yield of solid phase of any given I.P.T. melting point within the range investigated may be readily ascertained therefrom. Suppose, for example, that the theoretical yield of solid phase of I.P.T. melting point V' is required. This I.P.T. melting point is represented by V on the solidus curve *AC*. It is assumed, of course, that the liquid phase has been removed in an infinitely large number of stages over the temperature range $(y - a)$, and the melting points of the phases removed must cover the range from *D* to *K*. The total liquid phase removed has an I.P.T. melting point w' corresponding to W on curve *DG*. The yields of solid and liquid phases to be obtained from the original stock, represented by the point S_2, are calculated as in the one-stage removal. The ratio of solid to total blended liquids, is given quantitatively by the relation $(S'' - W'') : (V'' - S'')$, from which

$$\text{percentage yield of solid} = \left(\frac{S'' - W''}{V'' - W''}\right) \times 100$$

and

$$\text{percentage yield of blended liquids} = \left(\frac{V'' - S''}{V'' - W''}\right) \times 100$$

It must be emphasized that, owing to the experimental difficulties involved in the determination of these curves, only an *approach* to the actual curves representing the change in I.P.T. melting point of the solid phase during the infinite-stage removal of the liquid phase, has been obtained.

The authors have to thank the staff of the Anglo-Iranean Oil Co.'s Llandarcy refinery for their help in supplying materials used in carrying out this work.

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THE HYDROGENATION OF PETROLEUM FRACTIONS, EMPLOYING A LARGE PERCENTAGE OF CATALYST.*

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In the graphical-statistical method of anlysing hydrocarbon mixtures, as evolved in recent years in the laboratory for Chemical Technology at the Technical University of Delft,[1] it is often necessary to convert certain fractions by hydrogenation into a completely saturated hydrocarbon mixture. Not only is olefinic unsaturation, such as may occur in cracked distillates, removed in this hydrogenation [2] but at the same time the aromatic hydrocarbons are also converted into completely saturated products.

The process is usually carried out by heating the petroleum fraction to be examined with 10—20 per cent. by weight of nickel on kieselguhr (1 nickel: 5 kieselguhr) in rotating autoclaves with hydrogen under high pressure. The temperature used for this purpose is generally between 250° and 285° C. It has been demonstrated by special research that in normal cases only saturation of the hydrocarbons occurs.[3] There is no destruction, and the hydrocarbon mixture undergoes no change either in the number of rings or in the degree of branching. It is obvious that if there should be any doubt with respect to the latter, we must make sure that the hydrogenation carried out under high pressure has solely caused saturation of unsaturated constituents, so that no side reactions have taken place.

If the catalytic hydrogenation under high pressure, as described above, is applied to synthetic products, such as obtained in the polymerization of pure unsaturated hydrocarbons or as by-products in alkylation processes, the nickel catalyst usually employed will as a rule not decline rapidly in activity. The position is different, however, in the case of products containing components which cause a marked falling off in the activity of this catalyst. Various fractions obtained by the distillation of natural petroleums contain such deleterious components. Various sulphur compounds are undoubtedly to be regarded as such, and it is also advisable for other reasons, to remove such sulphur from the mixture. As a matter of fact, it is actually to be regarded as an advantage of catalytic hydrogenation with nickel, that as a result of the sulphur being bound by the catalyst the reaction products formed, if not free from sulphur, contain very little of this element. As a result, we obtain by catalytic hydrogenation under high pressure, saturated hydrocarbon mixtures which can easily and rapidly be examined by the graphical-statistical method referred to above. Furthermore, these products are completely colourless, and as far as the lower fractions are concerned, homogeneous oils; the higher fractions, though likewise completely colourless, may be solid or semi-solid owing, for instance, to paraffin wax separating out.

If, prior to hydrogenation, the sulphur contents of the oil fractions to be

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examined are very high, it should be determined in each individual case what effect this removal of sulphur has with respect to the structure of the molecular complexes deprived of their sulphur.

Wherever the activity of the catalyst is reduced by the presence of deleterious components, the number of times the catalyst has to be renewed may become so great as to hamper seriously the practical application of catalytic hydrogenation.

The authors have succeeded in eliminating this difficulty by adopting a different method, utilizing a very large quantity of catalyst.

Experimental Section.

In this investigation we used a large number of fractions obtained by distillation *in vacuo* from crude oils freed from their lighter components by ordinary distillation. Below a description will be given of some experiments with fractions of a Venezuelan petroleum. These fractions will be indicated by the numbers III, IV, and V (cf. table).

Fraction IV was at first hydrogenated at a maximum temperature of about 280° C. with 10—17 per cent. by weight of nickel on kieselguhr. This catalyst contains 5 parts by weight of kieselguhr to 1 part by weight of nickel. The hydrogenation was found to proceed extremely slowly, despite the fact that for each treatment the catalyst was invariably replaced by fresh material. No less than twenty-six times was fraction IV subjected to this hydrogenation with hydrogen under high pressure. Each time the autoclave containing the oil was raised to the maximum temperature of approximately 280—285° C in about 1 hour. Thereafter there was scarcely any further drop in pressure.* After each such hydrogenation the autoclave was cooled. Strange to relate, despite the twenty-six successive treatments, the oil fraction was far from being completely hydrogenated. In the meantime we had learnt from other experiments that this catalytic hydrogenation under high pressure could be considerably improved by using a much larger quantity of catalyst. Consequently, we now hydrogenated the oil—still incompletely hydrogenated after twenty-six treatments—a further two times with 100 per cent. by weight nickel on kieselguhr (1 nickel : 5 kieselguhr) at a maximum temperature of 300° C. with hydrogen under high pressure. It was surprising to find that the hydrogen was absorbed much more rapidly and that a completely saturated product was obtained. That this product was saturated is evident from the constants inserted in the table. The refractive index, n_D^{20}, of the product obtained after twenty-six treatments had fallen from $1{\cdot}5143^5$ to 1·5000. The specific gravity, d_4^{20}, had dropped from 0·9255 to 0·9018. The aniline point had risen from 62·2° C to 71·2° C. It will be seen from the table, however, that the complete saturation caused a further great change in the constants. The refractive index fell to 1·4778, the specific gravity to 0·8750, whilst the aniline point was about 20° C. higher than for the intermediate product obtained after the twenty-six treatments.

We would add that the specific dispersion, $\frac{n_{G'} - n_C}{d} \cdot 10^4$, became 154.

* Reduced to 0° C.

This is proof that the final product obtained could actually be regarded as completely saturated.[4] The aniline point read off from the graph of the aniline points for saturated hydrocarbon mixtures [4] was found to correspond, for the molecular weight of 303 and the specific refraction of 0·3234, with the experimentally obtained value (91° C). Further, this petroleum fraction contained an average of 2·2 rings per molecule, whilst it may be deduced from the values for the specific refraction and specific parachor that this oil has an average of four branches per molecule.

That the favourable result of the hydrogenation is really exclusively due to the large quantity of catalyst finally used was proved by the examination of two fractions, Nos. III and V (see table) obtained from the same Venezuelan petroleum. Employing each time 100 per cent. by weight of catalyst, we succeeded in completely saturating fraction III in three runs at about 280° C. (maximum temperature 290° C.). In the case of fraction V the same result was achieved after four treatments. Each treatment usually lasted 1 hr. at the operating temperature. The table also shows the constants for fractions III and V, both before and after hydrogenation. From the values given for the specific dispersion, as well as from the correlation between the aniline points read off in the graphs showing the aniline points for the respective molecular weights and specific refractions and those determined, it is once more evident that the products are completely saturated after hydrogenation. For the rest the results of the analyses for the fractions III, IV, and V, both before and after hydrogenation, are analogous.

In connection with this investigation the question arose, to what extent the use of the large quantity of catalyst would involve a risk of the products examined decomposing or changing their structure, since the large quantity of catalyst alters completely the consistency of the mixture of oil and catalyst. The product acquires the properties of a powder greasy to the touch, both before and after hydrogenation. In view of this fact we might expect, or at any rate we must take into account, the possibility of the product burning or becoming overheated. It has been proved experimentally, however, that in an analogous case this danger is non-existent. This was proved in the case of fraction V of another Venezuelan oil. The latter was hydrogenated by the old method. A thirteen-fold treatment was required, whilst when working with the large quantity of catalyst the completely saturated product was obtained after three treatments. It may be added that in the latter case the product was practically saturated after only two treatments. The physical constants showed the two products to be practically identical. It is to be expected, therefore, that in such cases the treatment with the large quantity of nickel catalyst will not give rise to decomposition processes or changes in structure.

By the above method it is also possible to convert asphaltic residues into mixtures of saturated hydrocarbons, the yields being good.

It is remarkable that the hydrogenation is so greatly accelerated by the use of the very large quantity of catalyst. It stands to reason that this result is important for hydrocarbon research. It is to be expected that in certain cases it will also be of technical significance. In this connection we have in mind those cases where the use of sulphur-resisting and poison-resisting catalysts in general is impossible. If it *is* possible to use these

poison-resisting catalysts at low temperature, it is unnecessary to adopt the above new method employing the very large quantity of catalyst.

In conclusion we should like to express our thanks to Mr. J. van Wijk, who carried out a considerable share of the experimental work.

Summary.

In the examination of hydrocarbon mixtures it is frequently necessary to saturate these mixtures completely by hydrogenation. If the hydrogenation is effected with a nickel catalyst, it is in many cases necessary with technical oil fractions to repeat the hydrogenation treatment many times, employing a fresh quantity of catalyst for each treatment.

*Fractions from Venezuelan Petroleum.**

	Fraction III.	Fraction III hydrogenated.	Fraction IV.	Fraction IV hydrogenated.	Fraction V.	Fraction V hydrogenated.
Molecular weight	248	255	304	303	353	351
n_C^{20}	1·4978	1·4689	1·5104	1·4753	1·5187	1·4817
n_D^{20}	1·5013	1·4712	1·5143	1·4778	1·5227	1·4843
n_F^{20}	1·5099 ?	1·4771	—	1·4839	—	1·4906
n_G^{20}	—	1·4820	—	1·4888	—	1·4956
$d^{20/4}$	0·9036	0·8635	0·9255	0·8750	0·9396	0·8880
$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ (0; 20° C.)	0·3262	0·3238	0·3254	0·3234	0·3250	0·3224
$(n_{G'}-n_C)\cdot 10^4$	—	131½	—	135	—	138
$\frac{n_{G'}-n_C}{d}\cdot 10^4$	—	152	—	154	—	155½
Aniline point:						
Determined, ° C.	58·1	83·5	62·2	91·1	67·0	97·3
Read off from the graph for saturated hydrocarbons, ° C.	—	82	—	91	—	97½
σ^{20} in dynes/cm.	30·91	29·79	31·97	30·60	32·58	31·55
$\frac{\sigma^{1/4}}{d}$ (20° C.)	2·609	2·706	2·569	2·688	2·543	2·669
Average number of rings from specific refraction:						
Per molecule	—	1·9[5]	—	2·2	—	2·6
Per molecular weight 100	—	0·7[5]	—	0·7	—	0·7[5]
Average number of rings from specific parachor:						
Per molecule	—	2·1[5]	—	2·6	—	3·1
Per molecular weight 100	—	0·8[5]	—	0·8[5]	—	0·9
Average number of additional branches:						
Per molecule	—	2	—	4	—	5
Per molecular weight 100	—	1	—	1 to 2	—	1 to 2

* Collection Chemical Technology tin No. 8.

We have now succeeded in considerably accelerating the catalytic hydrogenation under high pressure by using a very large quantity of catalyst (100 per cent. and more). The oil fractions examined showed no decomposition nor objectionable changes in structure. We thus succeeded in converting dark and even asphaltic oil fractions or residues into completely colourless saturated products by subjecting them a certain number of times to hydrogenation by the new method.

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